STANDARDS DEVELOPMENT BRANCH OMOE
36936000004694

PRINCIPLES OF SAMPLING AND ANALYSIS OF WASTE

FOR TCLP

UNDER ONTARIO REGULATION 347

Ontario

Ministry of the Environment
Laboratory Services Branch
February, 2002

TD
193
.T69
O56
1992
MOE

TD
193
.T69
O56
1992

Principles of sampling and
analysis of waste for TCLP :
under Ontario regulation 347 /

76905

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

Disclaimer

Although efforts have been made to ensure the accuracy of the information contained in this manual, the Laboratory Services Branch (LSB), Ontario Ministry of the Environment (MOE) does not assume liability for errors that may occur. The mention of trade names or commercial products in this document is for illustration purposes only and does not constitute endorsement or recommendation for use by MOE. This manual does not supercede the most current Ministry policies and procedures but may be used for guidance when needed.

Acknowledgments

This document was prepared by staff of the MOE–LSB. As the authors have used reference materials published in previous MOE reports and other sources, we are indebted to the authors of those documents. These publications are listed in the *references* section. We also wish to thank the individuals who provided comments in the preparation and review of this document.

Comments on this document can be sent to:

Ontario Ministry of the Environment
Laboratory Services Branch
Customer Services Section
125 Resources Road
Etobicoke, ON M9P 3V6

TABLE OF CONTENTS

1.0 INTRODUCTION 1
1.1 PURPOSE 1
1.1.1 Representative Samples 1
1.2 SCOPE 2

2.0 FIELD SAMPLING 3
2.1 INTRODUCTION 3
2.2 PLANNED SAMPLING EVENTS 3
2.3 SAMPLING 4
2.3.1 Procedural Approach 4
2.3.2 Sampling Techniques 4
❑ Staged Sampling Approach 4
❑ Simple Random Sampling. 4
❑ Stratified Random Sampling 5
❑ Sampling Using a Grid System. 5
❑ Systematic Sampling 7
❑ Judgement Sampling. 7
2.4 HOW AND WHAT TO COLLECT DURING FIELD SAMPLING 7
2.4.1 Avoiding Sample Contamination. 8
2.4.2 Mixing Composite Samples. 8
2.5 TYPES OF WASTE 8
2.6 SAMPLING FROM WASTE PILES. 9
2.6.1 Segregation of Mixed Piles. 9
2.7 CONTAMINATED SOLID WASTE STORED IN CONTAINERS 10
2.8 LIQUID WASTE. 11
2.8.1 Surface Liquid Leachate and/or Waste Water 11
2.8.2 Contained Waste. 11
2.9 LEAKING OR SPILLED WASTE FROM UNDERGROUND STORAGE TANKS 12
2.10 WASTE SITE ASSESSMENT. 13
2.11 SAFETY CONSIDERATIONS FOR SAMPLING. 13
2.12 SAMPLING EQUIPMENT. 14
2.13 SAMPLING EQUIPMENT DETAILS 18
2.13.1 Liquid Waste Sampling Equipment. 18

❑ Coliwasa. . . . 18
❑ Pond Sampler. . . . 19
❑ Wheaton Dip Sampler. . . . 20
❑ Open Tube Sampler (Thief). . . . 21
❑ Stratified Sample (Thief). . . . 22
2.13.2 Equipment for Sampling Non-Aqueous Sample Types . . . 23
❑ Bucket Auger. . . . 23
❑ Scoop/Trowel. . . . 24
❑ Soil Coring Device/Silver Bullet Sampler . . . 25
❑ Power Auger. . . . 26
❑ Split Spoon Sampler. . . . 27
❑ Shelby Tube Sampler. . . . 28
2.13.3 Additional Samplers for Sediments/Sludges . . . 29
❑ Veihmeyer Sampler. . . . 30
❑ Ponar Dredge. . . . 31
❑ PACS Sludge Getter. . . . 33
❑ PACS Grab Sampler. . . . 34
❑ Sludge Judge. . . . 35
❑ Hand Corer. . . . 36
❑ Gravity Corer. . . . 37
2.13.4 Samplers for Containerized Solids and/or Waste Piles . . . 38
❑ Grain Sampler. . . . 39
❑ Waste Pile Sampler. . . . 40
❑ Sampling Trier. . . . 40
2.14 EQUIPMENT CLEANING PROCEDURE. . . . 40
2.15 SAMPLE CONTAINERS. . . . 41
2.16 SAMPLE SIZE. . . . 41
2.17 SAMPLE HOLDING TIMES. . . . 42

3.0 LABORATORY ANALYSIS . . . 43
3.1 QUALITY MANAGEMENT (QM). . . . 43
3.1.1 Quality Assurance and Quality Control (QA & QC) . . . 44
3.2 DOCUMENTATION AND RECORD KEEPING. . . . 44
3.2.1 Methods and Bench Procedures . . . 44
3.2.2 Analytical Control Status. . . . 44
3.2.3 Chain of Custody. . . . 45
3.2.4 Analytical Records. . . . 45
3.2.5 Quality Control Sample Records. . . . 45
3.3 PRINCIPLES OF ANALYSIS AND METHODOLOGY. . . . 45

3.3.1 General Principles. . . . 45
3.3.2 Cleaning Procedures. . . . 46
3.3.3 Sample Holding Times. . . . 46
3.3.4 Analytical Turnaround Time. . . . 47
3.3.5 Instrument Calibration and Linearity. . . . 47

3.4 LABORATORY METHODS. . . . 47
3.4.1 Method Detection Limit. . . . 48
3.4.2 Precision. . . . 48
3.4.3 Accuracy and Recovery. . . . 48
3.4.4 Reference Materials. . . . 49
3.4.5 Method Run Control - QC Samples. . . . 50
3.4.6 Instrument and Matrix Controls. . . . 51
3.4.7 "Run" Description. . . . 51
3.4.8 Analytical Control Status. . . . 51
3.4.9 Qualitative Identification Criteria. . . . 52
3.4.10 Interferences. . . . 52
3.5 DATA ACCEPTANCE AND REPORTING 52
3.5.1 Data Acceptance Criteria. . . . 52
3.5.2 Data Reporting and Certificate of Analysis. . . . 52
3.5.3 Reporting Remarks - General. . . . 53
3.6 INTERPRETATION OF WASTE LEACHATE DATA. . . . 54
3.7 GUIDANCE ON SELECTING LABORATORIES FOR ANALYSIS 54

4.0 DATA QUALITY OBJECTIVES & LSB METHODS FOR TCLP LEACHATES 55
4.1 VOLATILE ORGANICS. . . . 55
4.2 ORGANOCHLORINE PESTICIDES AND PCBS. . . . 56
4.3 ORGANOPHOSPHOROUS PESTICIDES. . . . 57
4.4 CHLORPHENOLS (CPS) & PHENOXY ACIDS (PAS). . . . 58
4.5 CRESOLS, 2, 4-DINITROTOLUENE AND NITROBENZENE 59
4.6 UREA DERIVATIVE. . . . 60
4.7 TRIAZINES. . . . 60
4.8 CARBAMATES. . . . 61
4.9 GLYPHOSATE. . . . 62
4.10 QUATERNARY AMMONIUM COMPOUNDS. . . . 63
4.11 BENZO(A)PYRENE. . . . 63
4.12 DIOXINS AND FURANS - TOXIC EQUIVALENT QUANTITY 64
4.13 N-NITROSODIMETHYLAMINE (NDMA). . . . 65
4.14 METALS. . . . 66

4.15 URANIUM 66
4.16 BORON 67
4.17 ARSENIC/SELENIUM 68
4.18 MERCURY 68
4.19 NITRATE + NITRITE 69
4.20 FLUORIDE 70
4.21 NITRILOTRIACETIC ACID (NTA) 71
4.22 CYANIDE 72
4.23 PYRIDINE 73
4.24 Characterization of Extractable Organics in Water, Waste, and Soil by Gas Chromatography–Mass Spectrometry (GC/MS): LSB Method E3186 73

5.0 REFERENCES 75

APPENDIX A1 ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL) 77
A1.1 Introduction 78
A1.2 Definition 78
A1.3 Scope and Application 79
A1.4 Organic Analytes (Analytical Test Groups 16-24, 26 and 27) 79
A1.5 Conventionals, Metals and Inorganics (Test Groups 1-15 and 25) 81
A1.6 Procedure for LMDL Determination 81
A1.7 Treatment of Outliers 83

APPENDIX A2: EQUIPMENT DIAGRAMS 87

1.0 INTRODUCTION

Effective March 31, 2001, Ontario Regulation 347 has been amended with Ontario Regulation 558/00. One of the amendments is the adoption of the United States Environmental Protection Agency (US-EPA) Method 1311 to produce leachate for the toxicity characteristic determination for organic and inorganic parameters. Any parameter equal to or exceeding the values in the amended Ontario Regulation 347, Schedule 4 concentration, makes the waste "leachate toxic" and subject to classification as such under the regulation.

1.1 PURPOSE

The purpose of this Guide is to provide information related to the sampling, analysis, quality assurance (QA) and quality control (QC) procedures required for safely collecting and handling potentially hazardous waste samples for use in the Toxicity Characteristic Leaching Procedure (TCLP), and the subsequent analysis of that leachate.

1.1.1 Representative Samples

Representative Sample is defined as "A sample that closely resembles, or is a subset of the population being measured. A representative sample is one that is collected and handled in a manner that preserves its original physical form and chemical composition and that prevents changes in the concentration of the materials to be analyzed or the introduction of outside contamination" (see Reference 16, pp 817–818). The overall objective of the sampling techniques and procedures outlined in this Guide is to help collect representative waste samples for planned sampling events. The waste may be stored in various forms, including drums, containers of various sizes, in piles or simply in a field. The procedures for collecting a representative sample are site–specific. The procedures outlined in this Guide focus on the majority of the situations that may be encountered.

Once a representative sample has been collected, adequate testing or analysis must be done on the sample to meet the requirements of the regulations pertaining to waste classification and management. The final objective in providing this analysis is to compare waste leachate contamination concentrations (mg/L) with the levels found in Schedule 4.

1.2 SCOPE

It is assumed that users of this Guide are experienced in environmental sampling protocols and analytical laboratory analysis. This document does not supercede Ministry of the Environment (MOE) policies or sampling training. Samplers should adhere to existing MOE policies and Certificate of Approval specifications.

A compilation of published sampling techniques for use in planned sampling events is included in this Guide. Where detailed methods or procedures are lacking, there is room for the sampler and analyst to use discretion, apply the best available techniques, and follow accepted scientific practices. The sampler and analyst are strongly encouraged to have a "think safety" attitude, pay attention to their senses and use all available help when handling waste. With hazardous waste samples, however, extra care must be taken to ensure the safety of everyone involved. High concentrations of contaminants can pose a health risk to staff taking and handling samples, and to laboratory staff.

The information provided in this document represents a synthesis from a variety of sources including MOE and the US-EPA. Much of the information is available from Internet web sites. Included also are the recommendations and conclusions reached through collaborative efforts of government, industry and private laboratory personnel. Although the authors acknowledge that the sampling techniques described here may be applicable to unplanned sampling events, the sampling of unplanned events is beyond the scope of this Guide.

2.0 FIELD SAMPLING

2.1 INTRODUCTION

This Guide describes principles for the collection and handling of waste samples for planned sampling events. A waste may be a liquid, solid or combination which, because of quantity, concentration, or chemical characteristics, may pose a potential hazard to human health or to the environment when improperly treated, stored, transported, disposed, or otherwise managed. No detailed explanation of how to choose the sample portion or how to operate specific sampling equipment is given; it is expected that sampling personnel are provided specialized training in these areas. No specific advice for unplanned events is intended, but the information presented may be generally helpful for such applications.

2.2 PLANNED SAMPLING EVENTS

Prior to sampling a site, the purpose and objectives of the sampling program should be clearly stated. Compilation of background information on site history, location of structures, storage areas and potential spills from which contamination may have occurred should be done prior to planning the sampling. Using the available background information, a sampling plan design that is most appropriate for each specific situation can be developed. This may require that sampling take place on adjacent locations in order to check for off-site contamination or to obtain background levels. Provisions for feedback should be incorporated in the planning stage to allow for re-sampling, if necessary and possible.

During the planning phase, all the requirements of a proper field sampling program should be considered. The program should specify the sampling methods that are to be used for different types of samples. It should describe in detail the actual field collection and laboratory submission procedures to be used. The procedures should be standardized to the extent necessary to ensure comparability of results between sites, samples, sampling personnel, and between different laboratories and other stakeholders. The necessity of on-the-spot sampling decisions should be anticipated as much as possible and minimized. Planning for field sampling should result in sampling personnel having full knowledge of the following: sampling procedures and equipment to be used, observations to be recorded, methods of recording site locations, labeling of samples and containers, and proper procedures for storing and transporting samples to the analytical laboratory. The planning for sampling should

include considerations of all aspects of the safety of the sampling personnel, as well as of the environment.

2.3 SAMPLING

2.3.1 Procedural Approach

The two most common approaches to sample collection involve composite sampling or grab sampling. Either approach is applicable to the two types of sampling events: planned or opportunity. Planned samples are collected when sufficient time exists to consider all factors involved – including cost – and a sampling plan is designed to meet the data quality objectives (DQOs) of the study. On the other hand, samples of opportunity arise from events that were not generally anticipated, such as emergency response situations, and therefore could not be planned in advance. Unplanned sampling events often necessitate different sampling protocols and are not within the scope of this Guide. Waste samples may result from a discharge, a spill, or from dumping. When waste materials are transported – often by trucking – the waste may have to be sampled directly from the vehicle used. Sampling staff must ensure that samples represent the areas and depths of interest to each specific investigation, that sampling variability is properly determined and accounted for, and that there are a sufficient number of samples at the appropriate depths to fulfil the purposes of the sampling.

2.3.2 Sampling Techniques

- **Staged Sampling Approach.** A single–stage sampling approach results in all samples being collected and analyzed in one survey, while a multi–stage plan begins with an initial limited sampling plan to find the location of "hot spots", and/or to determine which chemicals are to be monitored. From the results of the initial sampling, additional sampling events are planned to define more precisely the areas of concern. Multi–stage sampling usually results in better characterization of a site compared to a single–stage approach; however, it generally will take more time to conduct. For this reason, multi–stage sampling may not be appropriate for the investigation of spills that require immediate attention.

- **Simple Random Sampling.** In this approach, all sampling locations are chosen in advance by random selection. This method is rarely used on its own, and would only be useful if there was no prior indication of

probable contaminant sources or distribution, if the soil types were uniform across the site, or if obtaining a uniform distribution of samples across the area was not important.

- **Stratified Random Sampling.** Areas that are likely to have higher concentrations of contaminants, or higher variability of contaminants (hot spots), are identified, (thus "stratifying" the design), then sampled, normally at a higher frequency than the other areas. Sampling within "strata" is properly randomized, as above. This method is used when prior knowledge of the site is sufficient to identify or flag those areas that are likely to be contaminated, or likely to be above the background concentrations. If done properly, stratification reduces sampling variability by separating out areas of high and low concentrations. Knowing the "hot spots" and picking them reduces the number of samples required. It defines the areas of greatest interest and provides for reduction of sampling in other areas.

- **Sampling Using a Grid System.** Using this system, a large site such as a landfill or field is divided into regularly spaced grids and the sample site locations either are selected randomly or chosen because of possible concerns such as a known "hot spot". Random sampling is often the preferred method where little or no previous information is available or where a number of sources of contaminants may exist. Stratification or layer sampling may be required as a modification in random sampling designs, in order to achieve statistical comparability of results among waste sample sites. Key factors for the application of grid sampling include the following:

- Where the investigation is directed toward a specific point-source discharge, a chosen sampling area design is the most common. Using this design, sampling stations are located in a grid or radiating pattern around the source.

  ii. The grid can be a regular grid based on lines intersecting at right angles, with sampling points located at the intersections. The spacing of the lines should be such that it provides adequate coverage of the area. The emphasis is on areas of waste.

iii. A radiating pattern can be used, with "spoke" lines (as in a bicycle wheel) radiating out from the source and intersecting arcs at right angles to these lines. The sampling locations are usually positioned at the intersections of these lines. The spacing of the lines should be based on existing knowledge of the site.

iv. The distance between stations, or the size of the sampling grid in a random or grid-based method depends on a number of factors, such as heterogeneity of the waste, the size of the area or site(s) under investigation. The larger the grid units, the fewer the samples taken.

v. Where the area studied is large, the grid areas will also be large. Therefore, each sample collected represents a large physical area, and may give erroneous results unless the area investigated has uniform sample characteristics.

vi. The use of a grid for sampling areas that have uniform physical characteristics can result in the collection of an excessive number of samples.

vii. Dividing the study area into a number of smaller sampling locations, and collecting replicate samples from each of these is a practical alternative to collecting a large number of samples at a single station. Cost and the amount of detail required will determine the number of stations needed.

viii. Where samples are collected from a field or large area using the grid system, the number of samples per station site is as follows: Composite samples are obtained by collecting a number of sub–samples which are then combined and homogenized. Preferably this can be done on–site using larger than required sample portions which are mixed together to make a homogeneous composite waste sample. An aliquot of the homogenate is taken for chemical analysis.

ix For the sampling of areas suspected of containing significant amounts of pollutants, composite samples should be done over an area that is meaningful with respect to the sampling objectives (i.e. if the purpose is to determine the extent of a spill that is to be remediated, the area

over which compositing occurs should be about the minimum size of area that the equipment being used can handle). For such cases, a larger number of replicates should be considered in order to clearly and accurately define the extent of the pollution. Composite sampling should not be done for volatiles, as volatile analytes would be lost during mixing.

- **Systematic Sampling**. Samples are collected in a regular pattern. This may be along specified radii, or on points of a grid. The pattern is chosen according to knowledge of the site. This method provides a better and more complete type of coverage of the area than the random methods.

- **Judgement Sampling.** In this sampling design, sampling locations are chosen solely on judgement, one location at a time. Known "hot spots" are targeted. The biases of the sampler become dominant in choosing locations. This method is useful when the sampler has excellent knowledge of the site and there is thought to be significant contamination present from specific sources. When this method is used, it is usually prudent to combine it with other designs.

2.4 HOW AND WHAT TO COLLECT DURING FIELD SAMPLING

Section 2.12 lists advantages and disadvantages of various sampling equipment that have been used for soil and waste sampling. The sampling plan should consider the type of material likely to be encountered on the site and match this with appropriate sampling devices.

Soil sampling for the determination of pollutants other than volatile organics should be conducted by combining a number of samples from the same depth of interest into one sample that is representative of both the identifiable sampling site and the depth increment. Samples that are combined into a single composite sample should normally be taken from locations that are no more than four meters apart (i.e., 2 m radius from the central point of the sampling site).

The objective of this composite sampling is to ensure that the sample best represents the volume of material nearest the point of interest. The distances between samples making up a composite are limited in order to prevent mixing of contaminated soil wastes with clean soils in the sampling area. Note that due to the difficulties of depth

sampling, in practice more samples will make up a composite sample where sampling is near the surface than will be the case for sampling for depth. For surface or near surface soils, samples should be collected from within a 2 metre radius circle (or equivalent area), with a minimum of 10 cores or grab samples constituting the composite sample for analysis from each depth increment. Collection of blank and background control samples should be taken from nearby areas of similar soil type that are not suspected to be polluted.

2.4.1 Avoiding Sample Contamination

Waste soil sampling for organic contaminants requires careful attention in order to avoid contamination from other samples (cross-contamination), from sampling equipment, and from sample containers. For example, samples should be transferred directly from the sampling device to the storage container, where possible. Clean equipment should be used for each sample. Care must be taken to use the correct type of sample container for the specific pollutants to be determined (i.e. borosilicate glassware is not suitable for samples requiring boron analyses).

2.4.2 Mixing Composite Samples

The waste/soil cores or sample portions should be placed in a pre–cleaned stainless steel bowl and thoroughly mixed prior to being placed in the sample containers. The bowl and mixing spoon/rod are cleaned as per the usual wash/rinse procedure described in section 2.14.

2.5 TYPES OF WASTE

Wastes requiring TCLP are generally solid in nature, but liquid wastes are also possible. The following are examples of various types of waste and locations where sampling for TCLP analysis may be required:

- ❑ liquid waste
- ❑ truckload of waste
- ❑ tanker truck of waste
- ❑ open fields
- ❑ soil or non–liquid waste
- ❑ containerized liquids
- ❑ waste piles
- ❑ sediment
- ❑ containerized solids
- ❑ sludge
- ❑ landfill sites

2.6 SAMPLING FROM WASTE PILES

In some situations it may be necessary to obtain samples from large piles of solid waste materials. Sampling and testing of waste contaminated material in piles requires segregation of the various types of materials, representative sampling of the segregated piles and statistical analysis of the results.

To obtain representative samples from a large waste pile may pose problems due to the difficulty of obtaining subsurface samples. Surface samples are usually not representative of the entire pile, as some materials have a tendency to segregate into fine and course fractions over time as the waste pile is formed. The preferred method of sampling piles is for composite samples to be obtained which represent known locations within the pile. Enough sample should be taken at different depths to characterize the depth profile and the various layers. Normally, sites should be chosen in a properly randomized manner from locations in the pile, with the exception that known or suspected "hot spots" must be sampled. If the pile has a volume of less than three (3) cubic meters, then a minimum of three (3) aliquots are taken for each cubic meter of waste material and a composite analysis is done. For piles greater than three (3) cubic meters, take twelve (12) random samples and treat as individual grab samples.

Alternatively, for very large piles (more than about 5,000 cubic metres in size), the following formula could be used to determine the number of samples (N) required:

$$N = 31 + (\text{pile volume} - 5{,}000)/300$$

which means that piles consisting of 5,000 cubic metres require 31 samples to characterize the material, and larger piles require one additional sample for every additional 300 cubic metres of material. This formula is based on an early 1990's MOE document for Abandoned Sites and should be used with caution.

2.6.1 Segregation of Mixed Piles

Segregating waste contaminated materials into a variety of similar material type piles will help to minimize the number of samples required to properly characterize the mixed pile. An initial segregation may result in a better overall result because the separate component materials are probably not evenly distributed in the pile. If the bulk analysis is known or shows that the bulk level (of each parameter), divided by 20, is less than the Schedule 4

leachate level, then TCLP would not have to be done on that material (because leachate analysis is performed on a 20× dilution of the raw material).

Waste materials may already be stored in piles which are often made of various types of materials (e.g., soil, sludge, rocks, concrete, asphalt, construction wood waste and metal waste/containers, etc.). For piles showing several mixed materials (i.e., more than 10% of any material types), the piles should be segregated first into various types of the material and if possible the level of pollution. The observance of a liquid spilled onto a solid may be an indicator of another waste type within the whole.

2.7 CONTAMINATED SOLID WASTE STORED IN CONTAINERS

Representative samples of solid waste found in containers are collected and analyzed as follows:

- If there is any residual liquid or sludge at the bottom of the container or lugger box, the aliquot taken from the bottom layer should include a representative sample of the liquid or sludge.

- Aliquots are taken from the top, middle and bottom depths of the waste, if a core sampling device can be forced through the contents. These three aliquots form a composite sample when mixed together. This approach is not suitable for waste that contains large rocks, broken cement, or other large solid objects. Procedures for using sampling equipment are described in section 2.12.

- As an alternative to the core sampling procedure, the contents of the container can be transferred to a contained flat surface where aliquots are collected from portions representing the top, middle and bottom layers of the contents of the container. When the sampling is finished, the waste contents are returned to the original container for later classification and proper management. Care must be taken to avoid spills or equipment contamination during the manipulation of the drum and its contents.
- Where waste containers may contain mixed materials such as soil, rocks, concrete, wood, and packaging materials, a container is considered to contain mixed waste materials if more than 10% of the content of the drum is of a different type than that remaining.

- ❑ For drums that have visible phase separation between liquids, solids, or between solid-liquid composites, each distinct phase must be sampled and analyzed separately.

2.8 LIQUID WASTE

Although most samples for TCLP analysis will be in solid form, liquid samples will occasionally be required to characterize the sample completely.

2.8.1 Surface Liquid Leachate and/or Waste Water

The term waste water, as used here, refers to the possibility of leachate from a seep or pond seeping into or draining, or running into adjacent waterways such as streams, ponds, lagoons, holding areas, or any site area where there appears to be a pool, or a seep. Liquid in the area of a waste pile, waste site, or the containment area holding run–off and leachate coming from or being generated from a potentially hazardous waste site area is also treated as liquid leachate. The liquid may be from the containment area of a landfill site or leachate that is leaking out. Most sampling requirements used for liquid leachate analysis can be fulfilled by manual sampling (i.e., grab sampling) using simple field equipment such as: buckets, funnels, bottles and pond sampler.

2.8.2 Contained Waste (Note: Only trained staff can sample drums & tanks)

Sampling liquid waste in drums, and large containers such as tankers, requires the liquid sampling techniques described in section 2.13. Large tanks may have a drain valve at the bottom, but the tank still has to be sampled from the top using a thief or other type of sampler in order to sample all phases that may be present and to minimize the chance of spillage. If only one phase can be seen, a glass thief sampler may be suitable; otherwise, some form of stratified sampling will be necessary.

A liquid spill to the ground has the potential to be contained if isolated immediately. A spill or leak from a container stored on soil will result in the soil being polluted. Such soil is sampled as solid waste using the appropriate equipment choice given in section 2.12.

Spills of hazardous waste may be small and easily contained, or may cover a large area that will require considerable effort to clean up. In the case of soil and land use, excavation may be required and this may entail the transport of several truckloads of waste. In order for this waste to be disposed, it must be classified under Regulation 347, which would require TCLP leachate preparation and comparison to Schedule 4, prior to being classified as solid, non-hazardous waste.

The type of liquid material stored in drums can vary significantly from drum to drum, and therefore sampling should be more extensive to ensure representativeness. All drums should be sampled from the top using a coliwasa sampler so that all phases present are represented in the aliquot taken. If only one phase can be seen, a glass thief sampler may be suitable.

Various types of waste may have a density different than that of water. In a mixture of water and waste in a container, some of the waste will tend to settle (i.e., cresol, methylene chloride) at the bottom of the drums or form layers within the sludge, while the lighter fraction (i.e., benzene) may be floating. Consequently, proper sampling of waste contaminated liquid or sludge in drums first requires a separation of the various phases or layers. The drums are allowed to rest in an upright position for the natural separation to take place.

When using a thief sampler, drums still have to be sampled from the top – to ensure all phases present are taken. The sediment, if it can be sampled, is treated as a solid waste. It is likely that multiple applications of a thief sampler will be required to collect sufficient sample to permit proper characterization of the drum contents. Separation of various layers may best be done by the laboratory performing the analysis. The volume of sample taken must be sufficient to allow for the determination of all required parameters plus associated quality control samples. Enough of the drum contents should be sampled to generate approximately 300 grams of material.

2.9 LEAKING OR SPILLED WASTE FROM UNDERGROUND STORAGE TANKS

If liquid waste has been stored in a manner similar to that used for fuel storage tanks, then similar sampling requirements are suggested if the waste container is found to be leaking or is being excavated and removed as hazardous waste. The polluted soil

surrounding the tank should be sampled by using a grid system, where soil samples are taken from each grid location. The container contents are sampled from the top using an appropriate device such a coliwasa or thief open tube sampler (see reference 17).

2.10 WASTE SITE ASSESSMENT

A large–area site such as a landfill or farm field may require the use of a grid system to map out sample site locations. The grid (see Section 2.3) size will determine the number of samples required. A grid system will ensure that a sufficient number of sampling locations are chosen. This necessitates that some sampling occur in areas believed to be pollution–free. The actual pattern and number of sample sites will depend on the methods chosen for interpreting the resulting data.

For a small–area site, a grid may not be required. Examples of a small–area site include a tank or other waste container, or a truckload of material en route to a drop off site or dumping area.

2.11 SAFETY CONSIDERATIONS FOR SAMPLING

Safety considerations should be included in any sampling plan. Taking samples of opportunity (section 2.3.1) may be especially hazardous, as they are not specifically planned for. The sampler should always recognize and appreciate the importance of performing personal hazard assessments before, during, and after sampling. The possible hazardous nature of the samples themselves, or of the sampling site, may not be apparent at the time of sampling. Even after samples have been collected and stored, they could still pose a danger to the safety of the sampler or to other personnel who may have close contact with the samples. Key considerations for the sampler to keep in mind are:

- ❑ proper methods of approaching and sampling a site
- ❑ generic steps in assessing personal risk
- ❑ possible health effects of hazardous materials
- ❑ requirements which must be met before entering a confined space
- ❑ methods that can be employed to minimize exposure to hazardous substances while sampling
- ❑ sampling safety equipment
- ❑ ministry policies and protocols
- ❑ storage and transportation considerations
- ❑ materials used to clean sampling apparatus are treated as hazardous waste

2.12 SAMPLING EQUIPMENT

The following types of sampling equipment can be used to cover most waste sampling applications. Diagrams of some of the equipment described below are shown in Appendix 2 [number in brackets is page number of corresponding diagram].

1. Coliwasa [88]
2. Pond [88]
3. Open Tube (Thief) [89]
4. Thief [89]
5. Wheaton [90]
6. Scoop or Trowel [91]
7. Coring Device [91]
8. Power Auger*
9. Split Spoon Sampler*
10. Shelby Tube Sampler*
11. Veihmeyer Sampler [92]
12. Ponar Dredge [93]
13. PACS Sludge Getter [93]
14. PACS Grab [98]
15. Sludge Judge*
16. Hand Corer [94]
17. Gravity Corer [94]
18. Grain Sampler [95]
19. Waste Pile Sampler [95]
20. Sampling Trier [96]
21. Shovel*
22. Pail*
23. Oakfield Sampler*
24. Bucket Auger [90]
25. Silver Bullet Sampler [92]
26 .Dipper [96]
27. Weighted Bottle [97]
28. PACS Wide-Mouth [97]
29. Open Tube [98]
30. Stratified Thief [99]

* denotes illustration not available

Refer to the following tables for equipment choices that best fit specific sampling activities.

Table 1 - Soil Sampling Equipment Summary			
Sampling Device	**Suggested Use**	**Advantages**	**Disadvantages**
Trier	Soft to firm surface soils	Easy to use and clean. Inexpensive	Difficult to use in Stoney soils, dry sandy soils or hard clays.
Trowel	Soft to firm surface soils	Easy to use and clean. Inexpensive	Difficult to use in hard clays. Difficult to obtain sample that is representative of a specified depth.
Tulip bulb planter	Soft to firm surface soils: 0 -15 cm	Easy to use/clean. Inexpensive. Uniform diameter and volume. Relatively undisturbed sample suitable for volatile analysis.	Suitable for only one depth. Difficult to use in hard soils or in dry loose soils.
Soil probe or corer (i.e., Oakfield Sampler)	Soft to firm surface soils: 0 - 60 cm.	Easy to use. Core is often relatively undisturbed and may be suitable for volatile analysis.	Limited depth capabilities. Difficult to use in hard, stony, or dry sandy soils. Difficult to clean sticky clays from parts of some devices.
Dutch auger, auger buckets	Surface soils to intermediate depths as deep as the device handle.	Will sample to greater depths than above equipment. Can be use in hard soil.	Depth is limited by soil conditions (stones and collapsing sidewalls). Soil mixing occurs during sampling; therefore, not suited to volatiles. Difficult to clean. Additional care must be taken to assure the sample is from the proper depth.
Hand held subsoil probes	Surface soils to intermediate depths.	As above. Maintains an undisturbed core. Suitable for volatiles.	Depth limited by soil conditions (stones and collapsing sidewalls)
Hand operated power auger	Soil, 15 cm - 5 m.	Good depth range. Useful in wide range of soils.	Soil is mixed by auger; therefore unsuitable for volatiles. Requires two or more operators. Requires a gas powered engine, therefore potential for sample contamination. Difficult to clean. Difficult to use when large stones or rocks present. Care required to assure sample is from desired depth.

Backhoe or power shovel	Soil 15 cm -5m	Good depth range. Wide area for sample collection within a horizon. Can collect undisturbed sample.	Expensive relative to above methods. Highly disruptive. Fuel or hydraulic fluid leaks could contaminate the immediate sample area.
Split Spoon Sampler	Soil 0 cm - bedrock.	Excellent depth range. Maintains reasonably undisturbed core suitable for volatiles. Useful in hard soils.	Relative to surface methods, is expensive. Requires two or more operators.
Thin-Walled (Shelby tube) sampler	Soft soil 0 cm - bedrock.	Excellent depth range. Maintains undisturbed core suitable for volatiles.	Not durable in rocky soils. Sample can be lost in very soft clays or loose sands below water.
Further information: References 4, 8			

Table 2 provides suggested sampling equipment for non soil types of waste.

Table 2 - Table of Recommended Sampling Devices for Non–Soil Waste

Waste Type	Recommended Sampling Device	Limitations
Liquids, sludges, and slurries in drums, vacuum trucks, barrels and similar containers.	· Coliwasa Open Tube · Thief (stratified sample) · Open Tube	Not for containers more than 1.5 m deep.
	a) Plastic	Not for wastes containing ketones, nitrobenzene, dimethylformamide, mesityl oxide, tetrahydrofuran, or other organic liquids.
	b) Glass	Not for wastes containing hydrofluoric acid and concentrated alkali solutions.
Liquids and sludges in ponds, pits, lagoons, or treatment units	Pond	Cannot be used to collect samples beyond 3.5 m. Dip and retrieve sampler slowly to avoid bending the tubular aluminum handle.
Powdered or granular in bags, drums, barrels and similar containers.	a) Grain sampler	Limited application for solids sampling of moist and sticky solids with a diameter more than 0.6 cm.
	b) Sampling trier	May incur difficulty in retaining core sample of very dry granular materials during sampling.
Dry wastes in shallow containers and surface	Trowel or scoop	Not applicable to sampling deeper than 8 cm. Difficult to obtain reproducible sample portions.

Table 2 - Table of Recommended Sampling Devices for Non–Soil Waste		
Waste Type	**Recommended Sampling Device**	**Limitations**
Waste piles	Waste pile sampler	Not applicable to sampling solid wastes with dimensions greater than half the diameter of the sampling tube.
Solid deeper than 8 cm (3 in)	a) Soil auger	Does not collect undisturbed core sample.
	b) Veihmeyer sampler	Difficult to use on stoney, rocky, or very wet soil.
Wastes in storage tanks	a) Weighted bottle sampler	May be difficult to use on very viscous liquids.
	b) Bacon bomb	Volume restriction 1 L maximum.
	c) Kemmerer sampler	May need extra weight.
Further information: References 12, 13		

2.13 SAMPLING EQUIPMENT DETAILS

The following information was adapted from Reference 6, (Section 5).

2.13.1 Liquid Waste Sampling Equipment

Coliwasa

The coliwasa or composite liquid waste sampler is one of the most important liquid hazardous waste samplers. It permits the representative sampling of multi phase wastes of a wide range of viscosity, corrosivity, volatility, and solids content. Its simple design makes it easy to use and allows the rapid collection of samples, thus minimizing the exposure of the sample collector to potential hazards from the waste.

Three types of coliwasa samplers are made; plastic, PTFE and glass. The plastic type consists of a translucent plastic sampling tube. This type is used to sample most containerized liquid wastes except wastes that contain ketones, nitrobenzene, dimethylformamide, mesityl oxide, and tetrahydrofuran. The glass type uses a borosilicate glass plumbing pipe as the sampling tube and PTFE for a stopper rod. This type is used to sample all other containerized liquid wastes that cannot be sampled with the plastic coliwasa except strong alkali and hydrofluoric acid solutions.

Procedures for Use

1. With the sampler in the open position, insert it into the material to be sampled.

2. Collect the sample at the desired depth by rotating the handle until one leg of the T is squarely perpendicular against the locking block.

3. Withdraw the sampler and transfer the sample(s) into laboratory cleaned sample bottles.

Advantages

- ❑ simplicity of operation
- ❑ versatile

Disadvantages

- ❑ problems encountered with fluids of very high viscosity
- ❑ difficulty in cleaning

Pond Sampler

The pond sampler is used to collect liquid waste samples from disposal ponds, pits, lagoons, and similar reservoirs. The pond sampler consists of an adjustable clamp attached to the end of a two or three piece telescoping aluminum tube, or a long wooden handle that serves as the handle. The clamp is used to secure a sampling beaker or bottle. This sampler could be made from equipment found on hand. The tubes or broom handle can be purchased from most hardware or pool supply stores. The adjustable clamp and sampling beaker (PTFE, HDPE, glass or stainless steel) can be obtained from most laboratory supply companies. Basically this sampler is just a container fastened to the end of a pole.

Procedure for use

1. Assemble the pond sampler. Make sure that the sampling beaker or sample bottle and the bolts and nuts that secure the clamp to the pole are tightened properly, a bungee cord or rope could also be use to fasten the container to the end of the pole.

2. Slowly submerge the beaker into the sample area with minimal surface disturbance.

3. Retrieve the pond sampler from the surface of the liquid sample (water) with minimum disturbance.

4. Taking a clean sample bottle, remove the bottle cap and position it next to the dipper/sampler edge.

5. Empty the sample from the dipper container, slowly into the sample bottle. For volatiles fill the sample bottle to the top leaving no headspace.

Advantages

- ❑ costs little to make
- ❑ can be made up almost on the spot
- ❑ can sample or reach out to the pole length

Disadvantages

- ❑ very difficult to obtain representative samples from stratified areas
- ❑ difficult to decontaminate when very viscous liquids are encountered (in such cases, consider the bottle or sample bucket as disposable)

Wheaton Dip Sampler

The Wheaton Dip Sampler is a useful tool for sampling liquids in shallow areas. The sampler consists of a glass bottle mounted on a metal pole of fixed length. Attached to the bottle's screw cap is a suction cup mounted on another metal pole. When the sampler is lowered into the liquid or water sampling area to the required sampling depth, the bottle cap is opened (unscrewed) by turning the metal pole attached to the suction cup which holds the screw cap. Bubbles will be visible around the sample bottle as its air is replaced by the liquid being sampled. When the air bubbles have ceased, the cap is screwed back on to the bottle to seal it closed. The resulting sample contains only liquid taken from the desired depth.

Procedure for use

1. Assemble the sampling device in accordance with the manufacturer's instructions, or build a home made unit.

2. Operate the sampler several times in order to get familiar with it. Make adjustments to ensure that the cap unscrews off and on successfully. Be familiar with the force or torque required to turn the mechanism.

3. When ready to sample, submerge the sampler into the liquid at the entry point desired.

4. The handle length is known. Therefore insert to the depth required and open the bottle cap.

5. When air bubbles from the bottle have ceased, assume the bottle is full and close the bottle cap.

6. Retrieve the bottle and transfer the sample to pre–cleaned sample containers. Fill the volatiles bottle completely to the top, so there is no headspace.

Advantages

- ❑ sample bottle is not opened until the required depth is achieved
- ❑ sample bottle can be closed after collecting the sample
- ❑ sample is contained and not mixed when the bottle is retrieved
- ❑ unit is easy to operate

Disadvantages

- ❑ sampling depth is limited to the pole length
- ❑ equipment may be difficult to field wash if the waste is sticking to it
- ❑ transporting a long piece of contaminated equipment may be awkward in a small vehicle

Open **Tube Sampler (Thief)**

This sampling device is basically a hollow glass or rigid plastic tube which is anywhere from 1–3 meters in length. It generally has an inside diameter of either 6 mm or 12 mm, depending on the viscosity of the liquid to be sampled. The plastic open tube sampler (Thief) is used to sample most containerized liquid wastes except waste that contains ketones, nitrobenzene, dimethylformamide, mesityl oxide and tetrahydrofuran. The glass open tube sampler (Thief) is used to sample all other containerized liquid waste that cannot be sampled with the plastic open tube sampler except strong alkali and hydrofluoric acid solutions.

Procedures for Use

1. Insert the sampler into the material to be sampled to the depth desired.

2. Place gloved thumb securely over open end of tube and carefully withdraw the sampler.

3. Transfer sample into laboratory cleaned sample bottles by releasing thumb.

Advantages

- ❑ least expensive
- ❑ simplicity of operation
- ❑ versatile
- ❑ disposable

Disadvantages

- ❑ sample leakage
- ❑ small sample volume

Stratified Sample (Thief)

This sampler uses discs or wipers to hold stratified liquids in position while the tube is slipped past them. The wipers keep the inside of the tube from carrying portions of the upper fluid down into other layers. The plastic stratified sample thief is used to sample most containerized liquid hazardous waste except waste that contains ketones, nitrobenzene, dimethyloforamide, mesityl oxide and tetrahydrofuran. It is especially useful for highly viscous, stratified liquids.

Procedures for Use

1. Insert the sampler into the material to be sampled with the outer sheath raised to the open positions.

2. When the desired depth is reached, slide outer sheath down over the centre section.

3. Withdraw the sampler and transfer discrete samples into laboratory cleaned sample bottles.

Advantages

- ❑ simplicity of operation
- ❑ representative sample obtained in viscous, stratified liquids

Disadvantages

- ❑ plastic is not compatible with certain substances
- ❑ it may be difficult to transfer the sample to a sample container

2.13.2 Equipment for Sampling Non-Aqueous Sample Types

Sampling of non-aqueous matrices encompasses several different types of waste: from solids in drums and containers to soils and sludges. There are many factors involved when choosing the proper sampling equipment for each of these materials. The most important consideration is to obtain a representative sample of the waste. The following section covers sampling devices designed for specific materials such as soils, sediment/sludges and containerized solids/waste piles.

Soils can be sampled at the surface or below surface depending on the type of information required. Soils are typically divided into two categories according to depth: surface and subsurface. Which is used depends on the requirements of the sampling program. There are several different types of samplers that can be used to collect a soil sample at any depth.

Bucket Auger

This tool consists of a hard metal central shaft and sharpened spiral blades. When the tool is rotated clockwise by its T-handle, it cuts the soil as it moves forward and discharges most of the loose soil upward. Cutting diameters vary. The length is about 1 m, and can be increased with the use of extensions. Depending on soil characteristics there are three general types of augers available, e.g., sand augers, clay/mud augers, and augers for more typical mixed soils. These tools can be purchased from scientific or forestry equipment supply houses.

The auger is particularly useful in collecting soil samples at depths greater than 8 cm. However, this sampler destroys the structure of cohesive soil and does not distinguish between samples collected near the surface or toward the bottom. It is not recommended, therefore, when an undisturbed soil sample for volatile organics is desired. It should be noted that this exception does not include analysis of base neutrals, acid extractables, total petroleum hydrocarbons or total organic carbon.

Procedures for Use

1. Remove unnecessary rocks, twigs, and other non-soil materials from selected sampling point.

2. Attach the bucket and handle to an extension rod.

3. Begin turning the auger with a clockwise motion and continue until the desired sampling depth is obtained.

4. Use a second auger to collect the sample. The auger utilized for hole advancement is not acceptable for sample collection.

5. Transfer the sample into laboratory cleaned sample containers using a clean decontaminated stainless steel spoon or trowel.

6. When collecting samples at depths greater than 30 cm, it is advisable to discard 12 mm of material in top of the auger due to cave-in.

Advantages

- ❑ relatively speedy operation for subsurface samples

Disadvantages

- ❑ destroys soil horizons as it samples
- ❑ not recommended for sampling of volatile organics

Scoop/Trowel

The trowel or scoop can be used in collecting surface soil samples. They can also be used for a variety of other solid waste samples. A trowel looks like a small shovel. A laboratory scoop is similar to the trowel, but the blade is usually more curved and has a closed upper end to permit the containment of material. Scoops come in different sizes and makes. Many are coated with chrome paint which can peel off and get into the sample: these are unacceptable. Stainless steel scoops are preferred, however, scoops made from alternative materials may be applicable in certain instances.

Procedures for Use

1. At specified intervals, take small, equal portions of sample from the surface and immediately below the surface.

2. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ easy to use and clean

Disadvantages

- ❑ sometimes difficult to maneuver sample, particularly if placing sample into volatile organic vials

Soil Coring Device/Silver Bullet Sampler

The soil coring device and the silver bullet sampler are used when a core sample is desired. The soil coring device consists of a brass cylinder with a handle for turning. The bit of the corer is sharp plastic. A plastic collection tube which will hold a sample is placed on the inside of the brass cylinder. This device may be substituted for the soil auger if core analysis of depth profiles needs to be performed. A serious limitation of this instrument is the depth of the core is only half a meter. Also, the cutting edge of the coring devices is plastic and is unable to pass through very rocky or tightly packed soil.

The silver bullet sampler consists of a cylinder into which a borosilicate glass collection tube is inserted. The top of the sampler is fitted with a T-handle which is used to manipulate the sampler. The bit is changeable. The silver bullet sampler was designed to take core samples in peat substrates. Due to its design, it lends itself well to uses in hazardous waste sampling. It is versatile and can be used as a soil coring device because the body is adjustable to reach greater depth. Also, the silver bullet sampler has a serrated bit which allows the sampler to move through rocky or tightly packed substrate more easily.

Procedures for Use

1. Insert borosilicate collection tube into the sampler

2. Place the sampler in position with the bit touching the ground.

3. Press down on the T-handle while rotating the sampler clockwise.

4. After reaching the required depth, turn the sampler 360° counter clockwise and remove from the ground taking care not to lose any of the sample.

5. Remove the borosilicate glass collection tube and transfer to a laboratory cleaned sample container, or cap at both ends for sample shipment.

Advantages

- ❑ can be used in various substances
- ❑ core sample remains relatively intact
- ❑ bit is replaceable (on silver bullet sampler)

Disadvantages

- ❑ depth restrictions (soil coring device)
- ❑ not useful in rocky or tightly packed soils (soil coring device)
- ❑ only soil coring devices of stainless steel construction are recommended for collection of soils for chemical analysis

Power Auger

A power auger is used in conjunction with a bucket auger or similar sampling device to obtain a soil sample at depths greater than six inches. The power auger is composed of an auger flight with a cutting head, attached to a power device which turns the auger. Various sizes and types of power devices are available, from one man units to truck mounted units. Additional auger flights can be used to increase the depth obtainable by the unit. The power auger is used to drill just above the desired sampling depth. A bucket auger or similar device (smaller in diameter than the auger flight) is then used to obtain the sample.

Advantages

- ❑ reduces sampling time
- ❑ samples at depth easily obtainable

Disadvantages

- ❑ initial expense
- ❑ use of gasoline powered engine increases possibility of contamination of sample
- ❑ not useful in rocky soils
- ❑ extensive decontamination procedure (steam cleaning of drill rig and associated auger flights)

Split Spoon Sampler

A split spoon sampler is used to collect representative soil samples at depth. The sampler itself is a length of carbon or stainless steel tubing split longitudinally and equipped with a drive shoe and a drive head. These are available in a variety of lengths and diameters.

Procedures for use

1. Assemble the sampling device by aligning both sides of the barrel and then screwing the drive shoe with retainer on the bottom and the heavier head piece on top.

2. Place the sampler in a perpendicular position on the material to be sampled.

3. Drive the tube utilizing a sledge hammer or well rig if available. Do not drive past the bottom of the head piece as this will result in compression of the sample.

4. Record the length of the tube that penetrated the material being sampled and the number of blows required to obtain this depth.

5. Withdraw the sampler and open by unscrewing drive shoe and head and splitting barrel. If split samples are desired, a decontaminated stainless steel knife should be utilized to divide the tube contents in half longitudinally.

6. Transfer sample into laboratory cleaned sample bottles, or, into bowl for homogenization for non-volatile analysis using a stainless steel scoop or trowel.

Advantages

- ❑ easily available
- ❑ strong
- ❑ ideal for split sample collection
- ❑ preferred sampling device for volatile organic sample collection

Disadvantages

- ❑ requires drilling or tripod for deeper samples

Shelby Tube Sampler

A Shelby tube is used mainly for geologic information but may be used in obtaining samples for chemical analysis. The Shelby tube consists of a thin walled tube with a tapered cutting head. This allows the sampler to penetrate the soil and aids in retaining the sample in the tube after the tube is advanced (without excessive force) to the desired depth.

Procedures for Use

1. Place the sampler in a perpendicular position on the material to be sampled

2. Push the tube into the soil by a continuous and rapid motion, without impact or twisting. In no instance should the tube be pushed further than the length provided for the soil sample

3. Allow soils to swell in the tube for a few minutes.

4. Before pulling out the tube, rotate the tube at least two revolutions to shear off the sample at the bottom

Advantages

- ❑ inexpensive
- ❑ tube may be used to ship the sample without disturbing the sample
- ❑ provides core sample
- ❑ easily cleaned

Disadvantages

- ❑ sometimes difficult to extract sample
- ❑ not durable when encountering rocky soil

2.13.3 Additional Samplers for Sediments/Sludges

Factors that contribute to the selection of sediment/sludge samplers include the width, depth, flow, and the bed characteristics of the sediment/sludge waste to be sampled. In collecting sediment/sludge samples from any source, care must be taken to minimize the disturbance and sample washing as it is retrieved through the liquid column above. When retrieving a sample through a water column of four inches or more, and/or fast stream flows, it is necessary to use sampling equipment that is capable of capturing the sample to prevent the loss of fine sediments. Several samplers which are used for other types of non-aqueous sampling are useful for sediment/sludges. These include the scoop/trowel, sampling trier, bucket auger, soil coring device, silver bullet sampler, waste pile sampler, and split spoon sampler, which have all been previously described in this section. Additional characteristics of coring and grab samplers used for sediment sample collection are due to design characteristics.

Coring devices generally provide the most representative samples with the least bias, at least in soft substrates. Grab samplers are affected by sediment texture and the size of the sample will depend on how deep the sampler sinks into the sediment and on whether the sampler will rise upon closure of the jaws. Even though the surface area to be sampled will be the same, these two samplers do not always sample the same volume of sediment. With gravity coring devices a similar problem can be encountered where the sampler may sink down into the sediment. Core samples are directly comparable only if the volume of the sample can be closely controlled to ensure a similar depth is collected each time. However, grab samples are more cost effective since fewer samples are required to sample the same area of sediment.

Veihmeyer Sampler

The Veihmeyer sampler is recommended for core sampling of most types of soil. It may not be applicable to sampling stoney or very wet soil. The basic sampler consists of: 1.5 m tube, 3 m tube, Drive Head, tip A (general), tip B (deep soil), Drop hammer (6.8 kg), and a puller jack and grip.

Procedures for use

1. Assemble the sampler by screwing in the tip and the drive head on the sample tube.

2. Insert the tapered handle (drive guide) of the hammer through the drive head.

3. Place the sampler in a perpendicular position on the material to be sampled.

4. With one hand holding the tube, drive the sampler into the material to the desired sampling depth by the pounding drive head with the drive hammer. Do not drive the tube further than the tip of the hammer's guide.

5. Record the length of the tube that penetrated the material being sampled and the number of blows required to obtain this depth.

6. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.

7. Rotate the sampler at least two revolutions to shear off the sample at the bottom.

8. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head and rotate about 90°.

9. Withdraw the sampler by pulling the handle (hammer) upwards. When the sampler cannot be withdrawn by hand, as in deep sampling, use the puller jack and grip.

10. Dislodge the hammer from the sampler; turn the sampler tube upside down; tap the head gently against the hammer; carefully recover the sample from the tube and proceed with the technique appropriate for containerizing.

11. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ can achieve substantial depths with appropriate length of tubing
- ❑ various heads available for different soil types

Disadvantages

- ❑ very difficult to clean
- ❑ parts needed for sampler are not appropriate for certain analyses.

Ponar Dredge

The Ponar dredge is a clam shell-type scoop activated by a counter-lever system. The shell is opened and lofted in place and slowly lowered to the bottom. When tension is released on the lowering cable, the latch releases and the lifting action of the cable on the lever system closes the clamshell. Ponars are capable of sampling most types of sludges and sediments from silts to granular materials. They are available in a "Petite" version with a 232 cm^2 sample area that is light enough to be operated without a winch or crane. Penetration depths will usually not exceed several centimeters. Grab samplers, unlike corers, are not capable of collecting undisturbed samples. As a result, material in the first centimeter of sludge cannot be separated from that at lower depths. The sampling action of these devices causes agitation currents which may temporarily resuspend some settled solids. This disturbance can be minimized by slowly lowering the sampler the last half meter and allowing a very slow contact with the bottom. Collection of sludge or sediment samples must be done after all overlying water samples have been obtained.

Procedures for Use

1. Attach a cleaned stainless steel Ponar to the necessary length of sample line.

2. Measure and mark the distance to bottom on the sample line. A secondary mark, 1 meter shallower, will indicate proximity so that lowering rate can be reduced, thus preventing unnecessary bottom disturbance.

3. Open sampler jaws until latched. From this point on, support sampler by its lift line or the sampler will be tripped and the jaws will close.

4. Tie free end of sample line to fixed support to prevent accidental loss of sampler.

5. Begin lowering the sampler until the proximity mark is reached.

6. Slow rate of descent through last meter until contact is felt.

7. Allow sample line to slack several centimeters. In strong currents more slack may be necessary to release mechanism.

8. Slowly raise dredge clear of surface.

9. Drain excess liquid through screen.

10. Lay dredge into a stainless steel or Teflon^{R} tray and open.

11. Collect a suitable aliquot with stainless steel spoon or equivalent and place into the appropriate sample container. Care should be taken to collect material which has not contacted the dredge's sides.

12. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ sample most sludges and sediments from silts to granular material
- ❑ light weight
- ❑ large sample can be obtained intact, permitting further subsampling

Disadvantages

- ❑ shock wave from descent may disturb fine sediments on the surface
- ❑ not capable of collecting undisturbed samples
- ❑ can lose pollutants when pulling samples through water column
- ❑ possible incomplete closure of jaws can result in loss of sample

PACS Sludge Getter

The PACS Sludge Getter can be used in very viscous material to collect a representative sample at depth. The Sludge Getter is an extra heavy duty grab sampler for heavy sludge areas. Its massive 15 kg weight and conical bottom allows penetration of extremely viscous materials. Constructed of type 316 stainless steel, it has a cup capacity of approximately 1000 mL.

Procedures for Use

1. Cover the sample vessel with the lid by maneuvering the handle on the sampler.

2. Lower the sample vessel to the desired depth.

3. Uncover the sample vessel using the handle, and allow the sample vessel to fill.

4. After the vessel has had time to fill, slide the lid back into place with the handle.

5. Remove sampling device from sludge.

6. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ can be used in heavy sludge
- ❑ can collect discrete samples at depth
- ❑ bag liner can be used with sampler
- ❑ easily decontaminated with steam cleaner or solvent wash

Disadvantages

- ❑ heavy

PACS Grab Sampler

The PACS Grab Sampler can be used to collect sludge samples from ponds, lagoons and containers. Grab samples can be obtained at discrete depths. For sludge sampling the PACS Grab Sampler is available with a wide necked bottle and large openings to allow the sample to enter the bottle. The sampler consists of a 1000 mL bottle that screws on the end of the 2 m. long handle. The control valve is operated from the top of the handle once the sampler is at the desired depth.

Procedures for Use

1. Assemble the sampler in accordance with the manufacturer's instruction.
2. Operate the sampler several times to ensure proper adjustment, tightness of the cap, etc.
3. Submerge sampler into liquid to be sampled.
4. When desired depth is reached, open sample bottle.
5. Retrieve sampler.
6. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ allows discrete samples to be taken at depth.

Disadvantages

- ❑ depth of sampling is limited by length of pole.
- ❑ not useful in very viscous sludges.
- ❑ difficult to decontaminate.

Sludge Judge

A Sludge Judge is useful for obtaining a core of sludge, or water and sludge. This may be useful in determining the physical state of a tank's contents or its volume of sludge. However, this device is commonly constructed of PVC and its use is limited in hazardous waste sampling due to possible reactivity and quality assurance considerations. The sludge judge is a long narrow tube with a check valve on the bottom.

Procedures for Use

1. Slowly insert the sampler into the material being sampled.

2. When the sampler has filled with material, pull back on the sampler to close the valve and retrieve the sample.

3. Transfer the sample (by pouring from the top or a release valve from the bottom) into a laboratory cleaned sample bottle.

Advantages

- ❑ easy to use
- ❑ delineates amount of settled sludge or physical state of medium

Disadvantages

- ❑ use is limited due to PVC construction
- ❑ difficult to decontaminate
- ❑ not useful in thick sludges

Hand Corer

This device is essentially the same type of thin-walled corer which is used for collecting soil samples. The corer has been modified by the addition of a handle to facilitate driving the core, and a check valve on top to prevent wash out during retrieval through an overlying water layer. Hand corers are more applicable to sludges but can be used for sediments provided the water is very shallow (a few centimeters). It should be noted, however, that this method can be disruptive to the water/sediment interface and might cause significant alterations in sample integrity if extreme care is not taken.

Some hand corers can be fitted with extension handles which allow collection of samples underlying a shallow layer of liquid. Most of the corers can be adapted to hold liners.

Procedures for Use

1. Decontaminate prior to use.

2. Force corer in with a smooth, continuous motion.

3. Twist corer and withdraw sample.

4. Transfer sample into an appropriate sample bottle with a stainless steel spoon or equivalent.

5. Transfer sample into laboratory cleaned sample bottles.

Advantages

- ❑ easy to use
- ❑ minimal risk of contamination

Disadvantages

- ❑ can disrupt water/sediment interface
- ❑ does not work well in sandy sediments

Gravity Corer

A gravity corer is a metal tube with a replaceable tapered nosepiece on the bottom and a ball or other type of check valve on the top. The check valve allows water to pass through the corer on descent but prevents washout during recovery. The tapered nosepiece facilitates cutting and reduces core disturbance during penetration. Corers are capable of collecting samples of most sludges and sediments. They collect essentially undisturbed samples which represent the profile of strata which may develop in sediments and sludges during variations in the deposition process. Depending on the density of the substrate and the weight of the corer, penetration to depths of 75 cm can be attained.

Care should be exercised when using gravity corers in vessels or lagoons that have liners since penetration depths could exceed that of substrate and result in damage to the liner material.

Procedures for Use

1. Attach decontaminated corer to the required length of sample line.
2. Secure the free end of the line to a fixed support to prevent accidental loss of the corer.
3. Allow corer to free fall through liquid to bottom.
4. Retrieve corer with a smooth, continuous lifting motion. Do not bump corer as this may result in some sample loss.
5. Remove nosepiece from corer and slide sample out of corer into stainless steel or PTFE (e.g., Teflon^{R}).
6. Transfer sample into appropriate sample bottle with a stainless steel laboratory spoon or equivalent.

Advantages

- ❑ collects undisturbed samples

Disadvantages

- ❑ may damage liners in vessels or lagoons

2.13.4 Samplers for Containerized Solids and/or Waste Piles

Waste materials are sometimes found on-site in containers or in waste piles. Containerized solids include powdered, granular, or coarse materials in drums, barrels, or other similar containers. Waste piles may be found in various sizes, shapes, structure and compactness. A few of the samplers commonly used for containerized solids/waste piles include scoop/trowel or the Veihmeyer sampler. The type of sampler chosen should be compatible with the waste so as to collect a representative material for proper analysis. Additional samplers may include the following: grain sampler, waste pile samplers and a sampling trier.

Grain Sampler

The grain sampler is used for sampling powdered or granular wastes or materials in bags, fiber drums, sacks, or similar containers. This sampler is most useful when the solids are no greater than 0.6 cm in diameter. This sampling device consists of two slotted telescoping tubes, usually made of brass or stainless steel. The outer tube has a conical, pointed tip on one end that permits the sampler to penetrate the material being sampled. The sampler is opened and closed by rotating the inner tube. Grain samplers are generally 61 to 100 cm long by 1.27 to 2.54 cm in diameter and they are commercially available at laboratory supply houses.

Procedures for Use

1. While the sampler is in the closed position, insert it into granular or powdered material or waste being sampled from a point near a top edge or corner, through the centre, and to a point diagonally opposite the point of entry

2. Rotate the inner tube of the sampler to the open position

3. Wiggle the sampler a few times to allow materials to enter the open slots.

4. Place in the closed position and withdraw from the material sampled.

5. Place the sampler in a horizontal position with the slots facing upward

6. Rotate and slide the outer tube from the inner tube.

7. Transfer sample into laboratory cleaned sample bottle.

Advantages

- ease of operation

Disadvantages

- not desirable for moist or sticky samples
- provides a low volume

Waste Pile Sampler

The Waste Pile Sampler is used for sampling wastes in large heaps with cross-sectional diameters greater than 1 m. It can also be used for sampling granular or powdered wastes or materials in large bins, barges, or soils where the grain sampler or sampling trier is not long enough.

This sampler is essentially a large sampling trier. It is commercially available but it can be easily fabricated from sheet metal or plastic pipe. A polyvinyl chloride plumbing pipe 1.52 m long by 3.2 cm in diameter by 0.32 cm wall thickness is adequate. The pipe is sawed lengthwise until the last 10 cm. The narrower piece is sawed off and hence forms a slot in the pipe. The edges of the slot and the tip of the pipe are sharpened to permit the sampler to slide into the waste material being sampled. The unsplit length of the pipe serves as the handle. The plastic pipe can be purchased from hardware stores.

Procedures for Use

1. Insert the sampler into the waste material being sampled at an angle of 0° to 45° from horizontal.

2. Rotate the sampler two or three times in order to cut a core of the material.

3. Slowly withdraw the sampler, making sure that the slot is facing upward.

4. Transfer the sample into a laboratory cleaned sample container with the aid of a spatula and/or brush.

Advantages

- ❑ easily fabricated
- ❑ disposable
- ❑ inexpensive
- ❑ can be fabricated to site specific needs

Disadvantages

- ❑ does not collect representative samples when the diameters of the solid particles are greater than half the diameter of the tube.

Sampling Trier

A Sampling Trier is used for sampling soils, powdered or granular wastes or materials in bags, fiber drums, sacks, or similar containers. A typical sampling trier is a long tube with a slot that extends almost its entire length. This tip and edges of the tube slot are sharpened to allow the trier to cut a core of the material to be sampled when rotated after insertion into the material. A spiral attachment may be used to advance a hole when sampling at depth. Sampling tiers are usually made of stainless steel with wooden handles. They are about 61 to 100 cm long and 1.27 to 2.54 cm diameter. They can be purchased readily from laboratory or forestry supply houses.

Procedures for Use

1. Insert the trier into the material to be sampled at a 0° to 45° angle from horizontal. This orientation minimizes the spillage of sample from the sampler. Extraction of samples might require tilting of the container.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. Transfer the sample into a laboratory cleaned sample container with the aid of a spatula.

Advantages

- ❑ preferred for moist or sticky samples

Disadvantages

- ❑ relatively difficult to use in stoney, dry or sandy soil
- ❑ if sample is excessively moist or loose and powdery, difficulty may be encountered when removing the sampler.

2.14 EQUIPMENT CLEANING PROCEDURE

The suggested decontamination or cleaning procedure for sampling equipment contaminated with waste is presented below. To do this cleaning in the field, use squirt bottles with wash solutions according to the following procedure:

1. wash and scrub with low phosphate detergent
2. rinse with tap water
3. rinse with 10% Nitric Acid solution
4. rinse with tap water
5. rinse with acetone or methanol followed by hexane
6. thoroughly rinse with clean water
7. air dry

Note: All rinses must be contained and disposed in an appropriate manner.

2.15 SAMPLE CONTAINERS

TCLP samples require 200 g of solid material to be submitted to the laboratory in a PET-500, Pack 5 bottle or glass jar with appropriate top. LSB recommends using bottles supplied by the laboratory performing the analysis. Bottles prepared by/for LSB are thoroughly cleaned and labeled and are also traceable to a specific lot number.

Sludge sample containers should never be filled more than ½ way to allow for gas formation. Note: Liquid samples taken for volatile analysis require a full container with no headspace. Use a separate 40 mL vial and store the full vial in a PET 500 bottle (in case the vial breaks or leaks under pressure).

2.16 SAMPLE SIZE

A minimum of 200 g of solid waste is needed to determine the percentage of solids, extraction fluid type and sample for extraction. If less than 200 g of solid sample is received, some parameters may not be analyzed.

2.17 SAMPLE HOLDING TIMES

The prescribed sample holding times from the Regulation are in the following table. The holding time is defined as the time in days from when the actual sample is collected from the waste site in the field until the TCLP extraction is performed. Sample(s) should be sent to the laboratory as quickly as possible to allow for the samples to be processed by the laboratory within the regulated number of days. Failure to generate leachate within the regulated times results in the inability to classify waste as solid, non–hazardous under the Regulation.

Table 3 -EPA Method 1311 Sample Maximum Holding Times	
Parameter	Number of days from field collection to TCLP extraction
volatiles	14
semi volatiles	14
mercury	28
metals	180

3.0 LABORATORY ANALYSIS

3.1 QUALITY MANAGEMENT (QM)

Quality Management is defined as: "That aspect of the over-all management function that determines and implements the quality policy." —International Standards Organization, ISO8402-1986.

Environmental analysis requires a sound quality management program in the field and laboratory to ensure the quality of data. Laboratory management is responsible for providing controls and performance evaluations, documenting the results, and taking action in a timely and cost efficient manner. A good quality management program includes the development of a quality assurance manual, regular use of external reference materials, participation in inter-laboratory (round-robin) comparison studies, and SCC (Standard Council of Canada) accreditation by an independent party such as the Canadian Association for Environmental Analytical Laboratories (CAEAL). Accreditation does not preclude the possibility of inspections to evaluate laboratory data. CSA standard Can/CSA Z753-95 and ISO Guide 17025 outline issues in implementing systems for managing staff, methods, equipment, samples and data.

3.1.1 Quality Assurance and Quality Control (QA & QC)

Quality Assurance: "All those planned and systematic actions necessary to provide adequate confidence that a product or service will satisfy given requirements for quality." —International Standards Organization, ISO8402-1986. Quality assurance encompasses activities that define the level of quality required and identify system components that affect quality, procedures for determining quality status, and the nature and timing of remedial action. A comprehensive quality assurance program will ensure that the quality of the process and its product are monitored, documented, and controlled on a continuing basis.

Quality Control: "The operational techniques and activities that are used to fulfil requirements for quality." -International Standards Organization, ISO8402-1986. Quality control encompasses activities that monitor and control laboratory tasks or systems to demonstrate that they meet predefined operating criteria or to substantiate the need for remedial action. These may include bench quality control, such as method blanks, certified reference materials, spiked samples and replicate samples, and run quality control, such

as standard reference materials, calibration, baseline, sensitivity, and curvature checks.

Performance Evaluation (PE) programs can evaluate and document the overall control status of the process and determines the need for long-term remedial action. Good Laboratory Practice (GLP) is a fundamental level of quality management (QM) in a laboratory. It includes good housekeeping, cleanliness, quality and consistency of supplies, availability of standard operating procedures for all routine activities, application of good technique based on proper education and training, and appropriate documentation of organizational and experimental purpose, procedures, observations, and conclusions or results. A laboratory can establish and maintain GLP and QM by adopting a standard code of practice such as those defined in Can/CSA Z753-95 and ISO Guide 17025.

3.2 DOCUMENTATION AND RECORD KEEPING

Essential elements of quality assurance and quality control are documentation and record keeping for all facets of sample handling and analysis.

3.2.1 Methods and Bench Procedures

The analytical method should be formally described in writing and authorized by the laboratory. Bench procedures should be documented in sufficient detail to ensure uniform application and must be readily available to technical staff. When modifications are required, they must be noted and appended to the appropriate analytical records. Bench procedures should include sample pretreatment, preparation, instrumental measurement methods, data reporting procedures, and all quality control activities. Bench procedures and methods should be reviewed periodically to ensure their continued applicability.

3.2.2 Analytical Control Status

Guidelines should be established to demonstrate that analytical systems are in control, or that corrective action is taken if they are out of control. Control limits should be established and maintained for calibration checks, method blanks, replicates or duplicates (for precision), reference material (for accuracy) and target parameter recovery. Results for all quality control samples should be closely monitored, and records should be kept of corrective actions taken when control elements are exceeded. All results of checks should be recorded and retained for future review.

Control charting is recommended to demonstrate control status for an extended time period and to help in assessing long-term performance. Analysts should participate in relevant inter-laboratory comparison studies to substantiate the over-all validity of their method. Balance accuracy should be confirmed by frequent checks with standard weights. Standard weights should cover the entire analytical range.

3.2.3 Chain of Custody

The laboratory should maintain submission documents to track the sample and sampling information for each sample submitted for analysis.

3.2.4 Analytical Records

An appropriate data-management system should be established and maintained within the laboratory providing analytical services. This system should ensure that records are readily accessible for auditing by the clients and by the Ontario Ministry of the Environment. Analytical results should be recorded and archived with the information required to ensure that all associated procedural, quality control and performance-evaluation records and the raw information they are based on can be traced back to their source.

3.2.5 Quality Control Sample Records

Laboratories should maintain in a secure manner all records necessary to show that the analytical systems used were in control at the time of analysis. The results of these quality control and performance-monitoring checks should be separately tabulated and summarized for ready retrieval, evaluation and auditing. A protocol should be established for data correction, including assurance that original data are legibly maintained.

3.3 PRINCIPLES OF ANALYSIS AND METHODOLOGY

3.3.1 General Principles

This section provides guidance on the general principles to be followed in sample preparation, cleanup and instrumental analysis. Analysis of waste leachate samples can be demanding and complex, depending on the sample type, matrix problems, the presence of co-extractive or interfering materials, and other considerations.

Laboratory analyses must conform to good laboratory practice as well as to requirements of Regulation 347, such as, leachate quality criteria given in Schedule 4.

The following are a few key principles that should be considered:

- Analysis should be carried out by competent laboratory personnel in a properly equipped and maintained laboratory environment;
- Analytical procedures should meet accepted principles of good laboratory practice and quality control and comply with the principles and guidelines for preparation and analysis listed in Section 4.
- Analytical techniques should be appropriate for the TCLP leachate and should lead to adequate separation and accurate identification of the parameters to be analyzed.

3.3.2 Cleaning Procedures

Each laboratory is responsible for ensuring that all glassware, reagents, and equipment used for sampling or analysis are free of contaminants and interfering substances. The frequency and type of equipment cleaning procedures used, and the manner by which equipment is 'proven' clean before use, are the responsibility of the laboratory. Cleaning might include a hot wash with phosphate-free soap, a hot rinse and a cold rinse, all using tap water, followed by a final distilled-water rinse. For specific requirements, refer to specific methods given in Section 4.

3.3.3 Sample Holding Times

As soon as a sample has been collected, some sample components can undergo changes in concentration by decomposition, volatilization, or by some other means. The rate of such changes depends on the individual pollutant. Consequently, to obtain analytical results representative of the original sample, some samples need to be analyzed within hours of being collected – whereas others can be analyzed weeks after being collected. All samples have a "shelf-life" or holding time, which designates the longest period of time that the sample can be held prior to analysis. If a sample is not analyzed within its stated holding time, the results may be considered invalid. EPA method 1311 specifies sample maximum holding times that may be different from those specified in the LSB methods.

3.3.4 Analytical Turnaround Time

The period of time between when samples are received by the laboratory and when their analytical results are reported is known as turnaround time. The standard turnaround time for most laboratories is two to three weeks. If requested, and at additional cost, laboratories can generally shorten turnaround time to meet specific project needs.

3.3.5 Instrument Calibration and Linearity

All analytical instruments should be calibrated in accordance with good laboratory practice (GLP). This includes periodic multiple-point calibration (full calibration series: a minimum of three standards) to establish response factors and linearity/working range. This should be established within the range normally encountered in samples of the type being analyzed.

The calibration should be checked by use of calibration-control standards prepared using a different source or manufacturer than that used to prepare the calibration standards. The linearity (working range) of the method for each analyte must be established and documented in the method. The linear range is the range of analyte concentrations over which the analytical system exhibits a linear relationship between the amount of material introduced into the analytical system and the instrument's response. No sample result should be reported that is outside the calibration range of the method. If a result is too high, the sample should be diluted. If too low, a larger aliquot of sample may be analyzed to meet the method detection limits required.

Calibration Verification and Standardization: Daily calibration checks using a subset of the full calibration series are required before each sample analysis series and should be repeated at intervals during the day to verify system stability and control. Documented evidence must be available to demonstrate the adequacy of the quality assurance and quality control practices for the preparation and verification of these standards.

3.4 LABORATORY METHODS

Ministry of Environment, Laboratory Services Branch methods are used in the analysis of TCLP leachate. A performance-based method system (PBMS) may be used, provided such methods meet the Data Quality Objectives given in Section 4.

3.4.1 Method Detection Limit

The method detection limit (MDL) is a statistically–defined decision point. Measured results greater than or equal to this point are interpreted to indicate the presence of analyte in the sample with a specified probability—usually greater than 99 per cent — assuming that sources of error in identification or biases in measurement are known and controlled.

MDLs must be determined for each target parameter. These should be calculated using the guidelines for Estimation of Analytical Method Detection Limits (see Appendix A1). The guidelines were established to ensure a consistent approach to the development of MDL estimates for the Municipal /Industrial Strategy for Abatement (MISA) Program. These MDLs should be established using the same sample size, sample preparation, and instrumental procedures that will be used for leachate analysis. They must be equal to or less than the Upper MDLs given in Section 4. The upper MDL is set at 1/10 of the Regulation 347, Schedule 4 limits. It is recommended that the determination of method detection limits be repeated at least every two years for each parameter to be analyzed, unless routine quality control data demonstrate that no significant change has occurred in the sensitivity or the precision of the analytical procedure. The MDLs should also be redetermined whenever a significant change is made to a method.

3.4.2 Precision

Precision is the degree of agreement among independent measurements of a quantity under specified conditions. Both within-run and between-run precision should be established. This can be done by using replicate sample analysis (within-run) and analysis of spiked blank samples or certified reference materials, if available (between-run). Control limits for these should be established and maintained as part of the analytical performance criteria.

3.4.3 Accuracy and Recovery

Accuracy represents the degree of agreement of individual measurements with an accepted reference value. Certified reference materials (CRMs), if available, can be used to assess laboratory accuracy. Recovery is the measured concentration of an analyte or surrogate added to a sample that is recovered by testing, and is generally reported as a percentage (% recovery).

3.4.4 Reference Materials

A Reference Material is a material or substance, one or more of whose properties are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. A Certified Reference Material (CRM) is a reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other document issued by a certifying body. CRMs for leachate for all Schedule 4 parameters are not currently available. Once such CRMs become available, these can be used to validate the performance of the leachate analysis method.

3.4.5 Method Run Control - QC Samples

Laboratory quality control sample analysis will monitor the performance of the methods, the instrumentation, and the analyst. The following are the types of quality control samples that are normally prepared and analyzed with each group of samples.

- Method Blank: A non–polluted sample of water, free of the target pollutants and any other substance that may interfere with the analysis; the method blank is processed exactly as the samples, including the addition of all appropriate reagents. Analysis of the method blank will establish a baseline response and indicate the presence of contamination in glassware and equipment and cross-contamination from samples containing high concentrations of target parameters or interfering substances.

  These results must be within acceptable limits based on collected data or data-quality objectives. Should method-blank results fall outside the established control limits, the results must be reviewed and validated or the samples in that particular run must be re-analyzed, accompanied by method blanks that fall within the control limits. If the blank values are outside control limits but do not contribute significantly to the total analyte concentration, (i.e., are less than 10 per cent of the lowest analyte sample concentration in the run) then corrective action may not be required.

- Duplicate Sample: A sample from which an additional portion is taken for re-analysis. If there is insufficient sample volume for replicate analysis, a duplicate sample may be collected and analyzed.

The analysis of a sample and its replicate should generally not be performed consecutively. Replicate-sample analyses will provide an indication of within-run precision.

- Spiked Blank: A method blank sample to which known quantities of target compounds have been added before processing. The concentrations added should be at or near the limits listed in Schedule 4 of Regulation 347. Analysis of spiked blank samples will indicate the efficiency of the method. These analyses may also be used to determine between-run precision.

- Spiked Sample: A sample to which known quantities of selected target compounds have been added prior to analysis. The spiked compounds must be recovered within tolerance limits established during method development. Results of spiked-sample analyses may show the presence of interferences that affect the accuracy of quantitation.

- Surrogates: Surrogates are typically stable–isotope labeled compounds with structural similarities to the organic analytes of interest; surrogates are not expected to be present in the environmental samples. An appropriate number of surrogates must be added prior to organic sample extraction and the result must be reported with the analytical data.

3.4.6 Instrument and Matrix Controls

The following additional quality control checks should be included as part of a well controlled system:

- Standard Control Check: Used to check instrument standardization. The check should be within an acceptable range (e.g., +/- 10 per cent of the expected values) established in method development. Failures may require re-standardization and re-analysis.

- Baseline Drift (Instrument Blank): Should be within tolerance limits based on data determined in method development. Failures may require re-standardization and re-analysis.

- Control Limits: All measurement systems are associated with random errors so that measured results – even when 'correct' – are associated with some variability. This variability is estimated by the standard deviation of results about the 'correct' value. From a statistical point of view, the measured value plus or minus a number of standard deviations defines a

range of measured values where a specified percentage of results are expected to fall. Control Limits can be set so that when measured values exceed set limits, the analytical system can be said to be no longer in statistical control, and the analyst must take action to bring the system back within control. In practice, control limits are generally set to ± 2 standard deviations (95% of results should fall) or ± 3 standard deviations (99% of results should fall).

3.4.7 "Run" Description

An analytical run is a group of samples processed together through each step of an analytical procedure. The number of quality control samples that should be analyzed depends on the number of samples in the analytical run and the analytical method.

3.4.8 Analytical Control Status

Protocols must be established for control limits and for corrective action when limits are exceeded. Quality control specifications are usually set at or above 95 per cent confidence level. By this definition, even in a well run laboratory, 5 per cent of a large enough set of routine results will fail this specification. Laboratories must identify and correct the source of error and apply corrective action, then re-analyze all samples associated with the failing QC check.

Control charting (instrument/run control QC samples) is recommended for demonstrating control status for routine, frequently used methods and for identifying trends and suggesting preventive measures. The number of analytes being monitored and charted for control will depend on the behavior of each analyte in a given laboratory. However, it is usual to demonstrate control of all analytes for at least one year, after which a few selected, representative analytes can be monitored and charted for control of an entire group. Data for the remaining parameters should be recorded and stored for future use.

3.4.9 Qualitative Identification Criteria

Qualitative identification criteria are crucial to assessing contaminants accurately and will vary depending on the analytical technique used. Document all relevant criteria used for identification, such as retention time, spectral wavelength, peaks for specific mass to charge (m/z) ratios and ion-abundance ratio requirements. These data must be documented in the method and be available on file for review.

3.4.10 Interferences

Interferences may be indicated by unacceptable spike recoveries (high or low) in environmental samples, especially when recoveries were good when testing clean samples such as blanks. There may be cases where interferences render detection of target analytes impossible. It is expected that the laboratory will make every reasonable effort to resolve and measure precisely every required parameter. However, limitations in the ability of a method to account for interferences may result in the inability to detect and quantify some analytes.

3.5 DATA ACCEPTANCE AND REPORTING

Although this section defines principles related to the acceptance and reporting of analytical data, it does not stipulate how those data must be developed, managed, or maintained within the laboratory record system. This leaves the flexibility to use systems and practices that best suit each specific organization.

3.5.1 Data Acceptance Criteria

The basis for determining the acceptability of laboratory data should include the following:

- ❑ The Data Quality Objectives as given in Section 4.0, are met.
- ❑ The results of all quality control samples that are applicable to the matrix and analyte group of interest (method blank, replicate and spiked blank as well as matrix controls) are within the statistically determined control limits. Commonly used limits are: ± 2 times standard deviation for warning limits and ±3 times standard deviation for control limits.
- ❑ The analyst must respond to any quality control results that exceed the control limits. Before data can be accepted, it must be demonstrated that the analytical systems are in control or that corrective action has been taken if they are out of control.

3.5.2 Data Reporting and Certificate of Analysis

A laboratory's data-management system should establish and maintain direct links between sample information (such as source, field sample number or code, date and time sampled, tests required), and laboratory information (such

as lab sample number or code, date and time analyzed, tests performed and identification of the analyst who did the work).

A properly recorded result should include the test or analyte name or code, the units of measure, the method used, and any qualifying remarks. If a non-official LSB method was used for analysis, a statement describing the method principle (sample processing and instrumental analysis) should be provided.

The number of significant figures in any result should be consistent with the number of significant figures appearing in the method. Analytical results may be corrected to take into account any positive results of associated method blank for some specific analysis. A method blank result above the method detection limit is normally considered a positive result. The criteria or control limits for blank corrections should be determined by laboratories on the basis of historical data, and these should be documented. Otherwise, data should be reported without correction. If a correction is made, it should be clearly identified and described. Data are not normally corrected for method recovery (for example, surrogates and spikes). All data (i.e. results or appropriate remark code) should be reported. Recoveries of any surrogates in organic analysis should be reported. The report should contain information about accuracy and precision estimates associated with the reported results where feasible.

3.5.3 Reporting Remarks - General

Analysts make every effort to control and prevent analytical and measurement errors, but certain samples may introduce analytical problems because of the presence of other matrix constituents. These may affect the quality and interpretation of the reported result. Remarks provide a means to bring these concerns to the attention of the data user. The following are instances where remarks may be included:

- Low-level or less than MDL: Report result < MDL or just < MDL

- Missing Data:
  - Data late: data not yet available
  - No data: laboratory accident
  - No data: insufficient sample volume
  - No data: no sample taken

- Sample Matrix Effects and Interference:
  - Interference suspected: use with caution
  - Multi phase sample: sample not homogeneous or not representative

- Approximate or Unreliable Data:
  Approximate value: because of nature of sample
  Approximate value: insufficient sample
  Approximate value: perishability effects
  Approximate value: interference suspected
  Unreliable: could not confirm by re-analysis
  Unreliable: improper container or container not filled to top
  Unreliable: possible lab QC problems
  Unreliable: sample decomposition noted
  Unreliable: analysis initiated after maximum storage time

- Miscellaneous:
  Sampling suspect: duplicates look different
  Sample identification questionable: labels do not match submission sheet
  Sample improperly preserved

3.6 INTERPRETATION OF WASTE LEACHATE DATA

If any parameter in a leachate from a single sample, or from the mean of duplicate/replicate samples, is greater than or equal to its criterion given in Schedule 4 of Regulation 347, as amended by Regulation 558/00, then the waste material from which the sample was derived is deemed to be a hazardous waste.

3.7 GUIDANCE ON SELECTING LABORATORIES FOR ANALYSIS

Laboratories participating in a recognized accreditation program, such as the one provided by the Standards Council of Canada through the Canadian Association for Environmental Analytical Laboratories (CAEAL), are recommended for this analytical work. A directory of accredited laboratories may be obtained from CAEAL, 265 Carling Ave., Suite 300, Ottawa, Ontario K1S 2E1. Phone (613) 233-5300, Fax: (613) 233-5501. This information may also be obtained from the Internet site at www.caeal.ca.

4.0 DATA QUALITY OBJECTIVES & LSB METHODS FOR TCLP LEACHATES

Data quality objectives for the TCLP leachate analysis, LSB methods and method principles are given in this section. A performance-based method system (PBMS) or alternative methods may be used. However, the methods must meet Data Quality Objectives given here. Screening methods, such as LSB method E3186 "The Characterization of Extractable Organics in Water, Waste and Soil by Gas Chromatography-Mass Spectrometry (GC/MS)" may be initially applied to leachate to identify organics. These compounds then can be quantitated by the methods given in Section 4. Leachates are produced by using the EPA Method 1311 for both organic and inorganic parameters.

4.1 VOLATILE ORGANICS

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Carbon Tetrachloride	0.5	0.05
Chlorobenzene	8.0	0.80
1,2-Dichlorobenzene	20.0	2.0
Tetrachloroethene	3.0	0.30
1,4-Dichlorobenzene	0.5	0.05
Trichloroethene	5.0	0.5
1,2-Dichloroethane	0.5	0.05
Chloroform	10.0	1.0
1,1-Dichloroethylene	1.4	0.14
Vinyl Chloride	0.2	0.02
Dichloromethane	5.0	0.5
Benzene	0.5	0.05
Methyl ethyl ketone	200	20

LSB Method: E3132 - The determination of volatile organohalides and hydrocarbons in water, leachates and effluents by headspace capillary gas chromatography (GC).

Method Principle: Leachate is analyzed by either headspace GC with MS detection (HS-GC/MSD) or purge and trap GC with MS detection (P/T - GC/MS) depending on concentration of sample based on screening by HS-GC/FID/ECD techniques.

4.2 ORGANOCHLORINE PESTICIDES AND PCBS

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Hexachlorobenzene	0.13	0.013
Hexachlorobutadiene	0.5	0.05
Hexachloroethane	3.0	0.3
Toxaphene	0.5	0.05
Aldrin + Dieldrin	0.07	0.007
Endrin	0.02	0.002
Chlordane (total)	0.7	0.07
DDT (total isomers)	3.0	0.3
Heptachlor + heptachlor epoxide	0.3	0.03
Lindane	0.4	0.04
Methoxychlor	90.0	9.0
Trifluralin	4.5	0.45
PCBs	0.30	0.03

LSB Method: E3400 - The determination of organochlorine pesticides (OCS) and other chlorinated organic compounds in water by hexane microextraction and gas chromatography - mass spectrometry (GC/MS)

Method Principle: An appropriate volume of leachate is extracted with 5 mL hexane. The extract is concentrated, reconstituted in toluene, and analyzed by gas chromatography/mass spectrometry (GC/MS) for target compounds.

4.3 ORGANOPHOSPHOROUS PESTICIDES

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Azinphos-methyl	2.0	0.2
Chlorpyrifos	9.0	0.9
Diazinon	2.0	0.2
Dimethoate	2.0	0.2
Malathion	19.0	1.9
Parathion	5.0	0.5
Methyl Parathion	0.7	0.07
Phorate	0.2	0.02
Temephos	28.0	2.8
Terbufos	0.1	0.01

LSB Method: E3389 - The determination of organophosphate pesticides in water by high performance liquid chromatography - ultraviolet (HPLC-UV) detection.

Method Principle: Samples are passed through pre-conditioned solid phase extraction (SPE) cartridges. Target analytes are eluted from the cartridge using ethyl acetate. The sample extract is evaporated to dryness and reconstituted in 1.0 mL acetonitrile prior to analysis by HPLC with UV detection.

4.4 CHLOROPHENOLS (CPS) & PHENOXY ACIDS (PAS)

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Pentachlorophenol	6.0	0.6
2,4,5-Trichlorophenol	400.0	40.0
2,4,6-Trichlorophenol	0.5	0.05
2,3,4,6-Tetrachlorophenol	10.0	1.0
Bromoxynil	0.5	0.05
Dicamba	12.0	1.2
Diclofop-methyl	0.9	0.09
Dinoseb	1.0	0.1
Picloram	19.0	1.9
2,4-D	10.0	1.0
2,4,5-T	28.0	2.8
2,4,5-TP (Silvex)	1.0	0.1

LSB Method: E3119 - The determination of chlorophenols and phenoxyacid herbicides in water by solid phase extraction (SPE) and gas chromatography- mass spectrometry (GC/MS)

Method Principle: Water samples are acidified (pH$\leq$ 2) and passed through pre-conditioned C_{18} solid phase extraction (SPE) cartridges. SPE cartridges are then dried and target compounds eluted using a small volume of solvent. The column elute is treated with diazomethane (to methylate target compounds), evaporated and finally diluted with solvent to 1.0 mL. This extract is analyzed by gas chromatography with a mass spectrometer (GC/MS). CPs and PAs are quantified as their corresponding anisoles and methyl esters, respectively.

4.5 CRESOLS, 2, 4-DINITROTOLUENE, AND NITROBENZENE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
m-Cresol	200	20
o-Cresol	200	20
p-Cresol	200	20
Cresol (Total) (when isomers cannot be differentiated)	200	20
2,4-Dinitrotoluene	0.13	0.013
Nitrobenzene	2.0	0.20

LSB Method: E3265 - The determination of acid/base and neutral compounds in final effluents and influents by gas chromatography-mass selective detection (GC/MSD).

Method Principle: This method consists of an in-situ acetylation and liquid/liquid extraction with dichloromethane. The extracts are dried using sodium sulphate and concentrated prior to instrumental analysis. The analysis is performed using a gas chromatograph-mass spectrometer (GC/MS) operated in the selected ion monitoring (SIM) mode.

4.6 UREA DERIVATIVE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Diuron	15	1.5

LSB Method: E3230 - The determination of phenyl ureas in water by high performance liquid chromatography-ultraviolet (HPLC-UV) detection.

Method Principle: Samples are solvent-extracted. The sample extract is dried, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by high performance liquid chromatography with UV detector.

4.7 TRIAZINES

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Atrazine + N-dealkylated metabolites	0.5	0.05
Cyanazine	1.0	0.1
Metolachlor	5.0	0.5
Simazine	1.0	0.1
Metribuzin	8.0	0.8

LSB Method: E3121 - The determination of triazine herbicides in water by gas chromatography/mass spectrometry (GC/MS).

Method Principle: Samples are made basic (pH>12) and solvent-extracted. The sample extract is dried, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by capillary gas chromatography/mass -spectrometry (GC/MS) for these target compounds.

4.8 CARBAMATES

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Aldicarb	0.9	0.09
Bendiocarb	4.0	0.4
Carbaryl	9.0	0.9
Carbofuran	9.0	0.9
Triallate	23.0	2.3

LSB Method: E3158 - The determination of carbamates in water by high pressure liquid chromatography - ultraviolet (HPLC-UV) detection.

Method Principle: Samples are solvent-extracted. The sample extract is dried, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by high performance liquid chromatography with a UV detector.

4.9 GLYPHOSATE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Glyphosate	28	2.8

LSB Method: E3415-The determination of glyphosate and aminomethyl-phosphonic acid in water and vegetation by high performance liquid chromatography-electrospray ionization-mass spectrometry (HPLC-EI-MS).

Method Principle: The glyphosate is derivatized with 9-fluorenyl methoxcarbonyl chloride (FMOC-Cl) to FMOC-Gly and then analyzed by HPLC/MS. The identification is achieved by establishing the HPLC retention time and the molecular ion of the reaction product (FMOC-Gly m/e 390) in negative electrospray ionization - mass spectrometry (ESI-MS). A confirmation ion of m/e 168 for glyphosate in also used.

FMOC-Gly is not available commercially and is prepared in-house. The quantitation of glyphosate is done by using a standard preparation in de-ionized water with FMOC in borate buffer.

Retention time of FMOC-Gly may shift. Therefore, standard addition of glyphosate into the final sample extract may be used for further confirmation of the identification of glyphosate.

4.10 QUATERNARY AMMONIUM COMPOUNDS

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Paraquat	1.0	0.1
Diquat	7.0	0.7

LSB Method: E3417 - The determination of diquat and paraquat in water, soil and vegetation environmental matrices by high performance liquid chromatography (HPLC) photodiode array and/or electrospray mass spectrometry (MS).

Method Principle: SPE cartridges are conditioned for the analysis using Ion-Pair reagents. A measured volume of leachate, is adjusted to pH 8.0 $\pm$ 0.5. The leachate is passed through the pre-conditioned SPE cartridge to isolate the analytes of interest. Analytes are desorbed from the cartridge using trifluoroacetic acid. Analysis is performed using LC-UV and/or LC-MS.

4.11 BENZO(A)PYRENE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Benzo(a)pyrene	0.001	0.0001

LSB Method: E3399 - The determination of polycyclic hydrocarbons (PAH) in aqueous matrices by liquid–liquid micro–extraction (LLME) and gas chromatography–mass spectrometry (GC/MS)

Method Principle: Samples are passed through pre-conditioned C_{18} solid phase extraction (SPE) cartridges. SPE cartridges are then dried and the target compound is eluted off the cartridges using an appropriate solvent. The eluate is concentrated and analyzed by gas chromatography with mass selective detector (MSD). A surrogate (d_{12}-chrysene) and internal standards (d_{10}-phenanthrene and d_{12}-benzo(a)pyrene) are added prior to sample extraction to monitor method performance.

4.12 DIOXINS AND FURANS - TOXIC EQUIVALENT QUANTITY

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Dioxins and Furans (TEQ)	0.0000015	0.00000015

LSB Method: E3418 - The determination of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and dioxin-like polychlorinated biphenyls (PCBs) in environmental matrices by gas chromatography-mass spectrometry (GC/MS).

Method Principle: Isotope dilution with mass spectrometric detection is used to determine the concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) in leachate samples. All leachates are fortified prior to sample extraction with known amounts of isotopically labeled PCDDs and PCDFs. All PCDDs and PCDFs are quantitated against these labeled standards. Sample extracts are cleaned using a 2-stage (silica/alumina) cleanup procedure.

4.13 N-NITROSODIMETHYLAMINE (NDMA)

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
N-nitrosodimethylamine	0.0009	0.00009

LSB Method: E3291 - The determination of N-nitrosodimethylamine (NDMA) in water by gas chromatography-high resolution mass spectrometry (GC-HRMS)

Method Principle: This method is designed to identify and quantify N-nitrosodimethylamine (NDMA) in water by adsorption onto Ambersorb 572, elution into an organic solvent and analysis by gas chromatography-high resolution mass spectrometry (GC-HRMS). The designation "GC" refers to high resolution (capillary column) GC.

The internal standard, d_6-NDMA, is added to the leachate. After the addition of Ambersob 572, the bottle is rolled at 50 rpm on a roller apparatus for 1 hour. The granular adsorbent is isolated by filtration on filter paper and allowed to air dry for 1 hour, minimum. The Ambersorb 572 is transferred to a 2mL autosampler vial and 400 µL of dichloromethane are added. The vial is capped and the contents are analyzed by GC-HRMS. NDMA is quantified by isotope dilution with d_6-NDMA.

4.14 METALS

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Lead	5.0	0.5
Barium	100	10
Cadmium	0.5	0.05
Chromium	5.0	0.5
Silver	5.0	0.5

LSB Method: E3094 - The determination of metals in final effluent, industrial waste and landfill leachates by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Method Principle: An aliquot of the digested sample is aspirated into the argon inductively coupled plasma discharge. The plasma serves as an atomization device as well as a source of excitation energy. The atoms emit their characteristic radiation and the energy of this radiation indicates the amount of analyte present. A computer-controlled spectrometer is used to analyze the plasma discharge.

4.15 URANIUM

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Uranium	10	1.0

LSB Method: E3216 - The determination of uranium in landfill leachate, industrial wastes and sewage samples by reflectance fluorescence spectroscopy (RFS).

Method Principle: Uranium in solution is deposited on a sodium fluoride pellet which is fused to produce UF_6. The fluorescence of UF_6 is measured by reflectance fluorescence spectroscopy. Method improvements are currently under review.

4.16 BORON

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Boron	500	50

LSB Method: E3073 - The determination of trace metals in soil, compost, liquid effluent and TCLP leachate by the Spectro inductively coupled plasma-optical emission spectrometer (ICP-OES)

Method Principle: The TCLP leachates are aspirated into an argon plasma which is a high energy source (approximately 8000°C). The plasma desolvates the aerosol, leaving salt particles for vaporization and atomization. The atoms move from a ground state into an excited state. When the atoms return to a lower energy state, photons are emitted at specific wavelengths. A spectrum is thus obtained. The spectrum is separated into component wavelengths by a diffraction grating and a photomultiplier detector measures the intensity of the light. The intensity of each emitted wavelength is proportional to the concentration of the particular element in the sample solution.

4.17 ARSENIC/SELENIUM

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Arsenic	2.5	0.25
Selenium	1.0	0.1

LSB Method: E3302 - The determination of arsenic, selenium and antimony in liquid industrial waste and landfill leachates by HYD-FAAS.

Method Principle: The determination of arsenic (As) and selenium (Se) entails digestion of samples in oxidizing acid mixtures, hydride generation, and atomization for measurement by flameless atomic absorption spectrophotometry (FAAS).

4.18 MERCURY

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Mercury	0.1	0.01

LSB Method: E3301- The determination of mercury in liquid industrial waste, landfill leachate and sewage samples by cold vapor-flameless absorption spectrophotometry (CV-FAAS).

Method Principle: Mercury in the sample is oxidized to its divalent ion form by an acid digestion procedure. The sample is then reduced by a stannous chloride solution to its elemental form. An air stream carries the mercury vapor into a flow through absorption cell positioned between a light source, set at 253.7 nM wavelength and a detector. The amount of absorption is proportional to the concentration of mercury in the sample.

4.19 NITRATE + NITRITE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Nitrate + Nitrite	1000.0	100.0

LSB Method: E3366 - The determination of ammonia nitrogen, nitrate nitrogen, nitrite plus nitrate nitrogen and reactive ortho-phosphate in water, sewage, leachate and industrial effluents by colorimetry.

Method Principle: Nitrate nitrogen plus nitrite nitrogen are determined as one of four automated nutrient tests which are performed simultaneously on the same aliquot of sample. Nitrate is reduced to nitrite by heating an aliquot of sample with hydrazine in alkaline media; this reaction is catalyzed by the addition of cupric ion. Subsequently, an azo dye is formed in acid media by diazotizing sulphanilamide with nitrite and coupling the product with N (1-naphthyl) ethylenediamine dihydrochloride. The absorbance of the light red azo dye is measured at 520 nm and the concentration of nitrate nitrogen plus nitrite nitrogen is determined by comparison with a similarly treated series of mixed standards.

4.20 FLUORIDE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Fluoride	150.0	15.0

LSB Method: E3172 - The determination of fluoride in water, leachates and effluents by automated ion chromatography.

Method Principle: Via Ion Chromatography (IC), fluoride is separated from other anions by using columns packed with ion exchange resin, and an eluent solution of sodium carbonate/sodium bicarbonate.

The sample is injected into the eluent stream and passes through a pre-column (AG-14). The pre-column removes any foreign matter entering the analytical system, which extends the life of the analytical column (AS-14). After separation, the anions are converted to their acid forms by ion exchange using a micro membrane suppresser, and their concentrations are determined from the conductivity of the fluoride produced. A conductivity meter measures the conductivity of each anionic species compared to the water background. Identities of the analytes are determined by their retention times.

4.21 NITRILOTRIACETIC Acid (NTA)

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Nitrilotriacetic acid (NTA)	40.0	4.0

LSB Method: E3406 - The determination of nitrilotriacetic acid (NTA) in aqueous samples by automated ion chromatography (IC).

Method Principle: Via ion chromatography (IC), nitrilotriacetic acid (NTA) is separated from other anions using columns packed with ion exchange resin and an eluent solution of sodium hydroxide. The eluent is passed through an anion trap column (ATC-1) to remove impurities which may be present in the working eluent solution.

The sample is passed through a cation trap column (in house design) made of Amberlite IR-120(H) resin to remove calcium, magnesium and iron from the sample matrix before analysis. The sample is then injected into the eluent stream and passes through a pre-column (AG-11). The pre-column removes any foreign matter entering the analytical system, extending the life of the separator column (AS-11). After separation, the anions are converted to their acid forms by ion exchange using a micromembrane suppressor and their concentrations are determined from the conductivity of the NTA produced. A conductivity meter measures the conductivity of each anionic species against the water background. The identities of the species are determined by their retention times.

4.22 CYANIDE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Cyanide (Total)	20.0	2.0

LSB Method: E3015 - The determination of free and total cyanide in environmental samples by calorimetry.

Method Principle: Total cyanide includes the free simple cyanides (such as HCN and KCN), and weakly bound cyanides (such as $Ni(CN)_4$), as well as those complexed cyanides that decompose to form free cyanides that distill out as HCN in an acidic environment. The automated determination of total cyanide exposes the sample to ultraviolet radiation to break down organic-metallic and alkali-complexed cyanide compounds to free cyanide. The distillation step isolates HCN under specific acidic conditions. The sequential combination of UV digestion plus distillation yields the measurement of "total cyanide". Interferences from thiocyanate are removed using a borosilicate glass coil in a UV-B chamber (wavelengths above 290 nM). When thiocyanate is not dissociated during UV digestion, it does not carry over in the distillation step. Cyanide is determined colorimetrically by the reaction of cyanide with chloramine-T to form cyanogen chloride which further reacts with a combination of barbituric acid and isonicotinic acid to form a highly colored coupling product, which is measured at 600 nM.

4.23 PYRIDINE

Parameter	Schedule 4 Limit (mg/L)	MDL (Upper Limit) (mg/L)
Pyridine	5.0	0.5

LSB Method: A semi–quantitative determination of pyridine is performed by using Method E3186 (see next page).

Method Principle: See Method E3186.

4.24 CHARACTERIZATION OF EXTRACTABLE ORGANICS IN WATER, WASTE, AND SOIL BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC/MS): LSB METHOD E3186

This method is intended to be a screening technique to characterize (identify) extractable organics in water, waste and soil by GC/MS. The extractable organics identified are reported according to their names or compound classes. The concentrations of sample components are approximate and are calculated relative to the specified internal standard. This is a semi-quantitative GC/MS method that provides data complementary to target compound analyses and is used to create or update target compound lists. It is not intended to be a total organic analysis.

Principle of the Method. The sample preparation procedure involves extraction of organic components from the specified sample type with a specified organic solvent, followed by concentration of the extracts. Instrumental analyses of the concentrated extracts are done by Gas Chromatography-Mass Spectrometry (GC/MS).

For a water or aqueous waste sample, the Internal Standard, d_{10}-phenanthrene, and the Surrogate Standards, d_3-2,4-dichlorophenol and d_6-NDMA, are added to an 800 mL aliquot of the sample. The pH is initially adjusted to approximately 10. The base/neutral (B/N) components are serially extracted with dichloromethane. The aqueous fraction is then adjusted to a pH of approximately 2. The acidic components are also serially extracted with dichloromethane.

For samples expected to contain low organic content, the B/N and acid fractions are combined, dried with anhydrous sodium sulphate and are subsequently concentrated by a rotary evaporator and a nitrogen evaporating unit. For samples expected to contain high organic content, the B/N and acid fractions are isolated, dried and concentrated separately. The concentrated extracts are analyzed by GC-(Full Scan)MS [(GC-(FS)MS].

For a soil or solid waste sample, the Internal Standard, d_{10}-phenanthrene, and the Surrogate Standards, d_3-2,4-dichlorophenol and d_6-NDMA, are added to the sample which is extracted with dichloromethane or toluene in a Soxhlet or Soxhlet/Dean-Stark apparatus, respectively. The concentrated extract is analyzed by GC-(FS)MS.

This method is specific for characterization analyses. The data from this method are complementary to the data from target compound analyses and can be used to create or update the target compound lists.

5.0 REFERENCES

1. Ontario Ministry of the Environment, MISA/Protocol for the Sampling and Analysis of Industrial/Municipal Waste Water, 1999, page 57 (Estimation of Analytical Method Detection Limits).

2. Ontario Ministry of the Environment, Sampling and Analysis of Wastewater for the 1999 Model Sewer Use by-Law, February 1999.

3. Ontario Ministry of the Environment, Protocol for Sampling and Testing at PCB Storage Sites in Ontario, January 2000.

4. Ministry of the Environment, Industrial Waste Sampling Procedures Manual, January 1989.

5. Hazardous Solid Waste Testing : First Conference, Conway/Malloy, editors, ASTM STP760.

6. New Jersey Department of Environmental Protection and Energy (NJDEPE), Field Sampling Procedures Manual, May 1992 order: Maps and Publications Sales Office Bureau of Revenue, CN 417, Trenton, New Jersey 08625, phone (609) 777- 1038.

7. Industrial Waste Sampling Procedures Manual, Waste Management Branch, January, 1989, copyright: Queen's Printer for Ontario, 1989. via Gilles Castonguay.

8. Conducting Environmental Compliance Inspections, U.S. Environmental Agency Region 10, Office of Environmental Assessment, Investigations and Engineering Unit. Contact Doug Smith, last update March 12, 1997. Web search: http://www.epa.gov/r10earth/offices/oea/ieu/manual/title.htm

9. Waste Analysis at Facilities That Generate, Treat, Store, and Dispose of Hazardous Wastes, A Guidance Manual, US EPA Solid Waste and Emergency Response (OS-520), OSWER 9938.4-03, April, 1994.

10. Environmental Sampling for Hazardous Wastes. ACS Symposium Series 267. Edited by Glen E. Schweitzer and John A. Santolucito, 1984.

11. ASTM D4687-87, Standard Guide for General Planning of Waste Sampling, ASTM, U.S. Printing Office, Washington, DC 20402

12. Ontario Ministry of the Environment, Sampling in the Environment, Course Notes, various authors, compiled by Human Resources Branch, Organizational Development and Learning Section.

13. Samplers and Sampling Procedures for Hazardous Waste Streams, EPA 600 2 80 018, January 1980. United States Environmental Protection Agency.

14. Web References:

    i. http://oaspub.epa.gov/webi/meta_first_new2.try_these_first.
    ii. http://www.epa.gov/epaoswer/hazwaste/ldr/resources.html#hazwaste
    iii. http://www.epa.gov/epaoswer/hazwaste/ldr/resources.html
    iv. http://www.frtr.gov/site/index.html

15. Principles of Environmental Sampling, 2nd Ed.; L.H. Keith, Ed.; American Chemical Society: Washington, DC, 1996.

16. Sampling, Processing and Analytical Procedures for Management of Excess Soil, Rock, and Like Materials; Ministry of Environment Draft Report, April 1995.

17. Guidance on Sampling & Analytical Methods for Use at Contaminated Sites in Ontario, Section 4.1 (Excavation Pits); Ministry of Environment Report (ISBN 0-7778-4056-1), July 1996.

APPENDIX - A1

ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL)
ONTARIO MINISTRY OF THE ENVIRONMENT

ANALYTICAL METHOD DETECTION LIMITS PROTOCOL
FOR
MUNICIPAL AND INDUSTRIAL STRATEGY FOR ABATEMENT PROGRAM

1999 Revision

APPENDIX A1
ESTIMATION OF ANALYTICAL METHOD DETECTION LIMITS (MDL)

The requirements listed in this section are specific to the Effluent Monitoring and Effluent Limits Regulations, but the principles listed here should be applied to all MOE programs involving low-level data.

A1.1 INTRODUCTION

This protocol has been established to ensure a consistent approach to the development of method detection limit (MDL) estimates for the MISA program based on the use of fortified reagent (blank) water or evaluation of available routine within-run duplicate analyses. The Effluent Monitoring and Effluent Limits Regulations have established criteria for maximum permitted laboratory MDLs (LMDLs), which are referred to as Regulation MDLs (RMDLs).

It should be noted that when MDL estimates are developed using clean samples (e.g. reagent (blank) water) they represent an optimum achievable value. MDLs obtained in this fashion are very useful for establishing performance criteria and allowing comparison of inter-laboratory method capabilities, but may not be applicable in defining the quantitation capability for other samples which introduce matrix effects.

The following protocol represents a modification to that documented in the Federal Register/Vol. 49, No. 209/Friday, October 26, 1984/Appendix B to Part 136 - Revision 1.11.

This modification restricts the options listed in the original document and gives more direct instructions at other option points.

A1.2 DEFINITION

The method detection limit (MDL) is a statistically defined decision point such that measured results falling at or above this point are interpreted to indicate the presence of analyte in the sample with a specified probability, and assumes that there are no known sources of error in identification or biases in measurement.

For the purposes of this protocol, the MDL is defined as having a confidence limit of 99%. This confidence limit defines the multiplication factor used from Student's t-tables relating MDL to the analytical precision. This Student's t-value depends on the

amount of data used to calculate the analytical precision. In general, analytical precision will depend on the analytical conditions and the sample matrix. When possible, precision will be determined by replicate analysis of typical low-level samples, with sufficient replication to provide a reasonable estimate.

A1.3 SCOPE AND APPLICATION

This protocol is designed for application to a wide variety of sample types ranging from reagent (blank) water fortified with a known concentration of analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The protocol requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

Because the MDL procedure was designed for application to a broad variety of physical and chemical methods, it was made device or instrument–independent.

There are four options available for estimating the analytical precision:

a) accumulation of a large number of in-run replicate analyses of typical samples at levels not exceeding 10 times the estimated MDL;

b) accumulation of in-run replicate analyses of laboratory reagent quality water spiked with a known amount of the target analyte(s) at levels not exceeding 10 times the estimated MDL;

c) analysis of eight replicate aliquots of a typical low level sample at levels not exceeding 10 times the estimated MDL;

d) analysis of a series of eight replicate aliquots of laboratory reagent quality water spiked with a known amount of the target analyte(s) at a level not exceeding 10 times the estimated MDL.

When applied for the Effluent Monitoring and Effluent Limits Regulations, the appropriate RMDL shall be used in place of the 'estimated MDL' in the above options.

A1.4 ORGANIC ANALYTES (ANALYTICAL TEST GROUPS 16-24, 26 AND 27)

This protocol requires that option d) in Section A1.3 be used. The fortification of laboratory reagent (blank) water with a known level of analyte is required to standardize the protocol for all laboratories and minimize the problems associated with analyzing duplicate or replicate samples or finding a standard "matrix" for

organics analysis. The analytical precision is established based on eight replicate analyses and the estimated MDL is derived from a combination of these measurements and the appropriate value from t-test tables. This option is not intended to assess the effect of the matrix on the values obtained but rather to define a standardized approach in the development and application of inter-laboratory performance criteria for the program.

❑ To determine the MDL, proceed as follows:

Make an estimate of the MDL using one of the following:

- the concentration value that corresponds to an instrument signal/noise ratio of 3:1;
- the concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water;
- that region of the standard curve where there is a significant change in sensitivity, e.g., a break in the slope of the standard curve;
- instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

❑ Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference-free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix. The use of commercially obtained or laboratory prepared organic free water is acceptable but clearly indicate what was used.

❑ Prepare a laboratory standard (analyte in reagent water) at a concentration which is at least 5 times, but not to exceed 10 times the estimated method detection limit. Proceed to Section A1.6.1.

A1.5 CONVENTIONALS, METALS AND INORGANICS (ANALYTICAL TEST GROUPS 1-15 AND 25)

This protocol allows any of the options a), b), c) or d) in Section A1.3 to be used. For options a) and b) the laboratory should review recent data on in-run replicates (data accumulated within the preceding 12-month period or less) and apply the formula as outlined in Section A1.6.3 to at least 40 data pairs.

- ❑ For option c) proceed as follows:

  - When a "real" sample is being used for the MDL determination analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated method detection limit proceed to Section 1.6.

  - If the measured level of analyte is less than the estimated method detection limit, add a known amount of analyte to bring the level of analyte between five and ten times the estimated method detection limit.

  - If the measured level of analyte is greater than 5 times the estimated method detection limit, there are two options:

  - Obtain another sample with a lower level of analyte in the same matrix if possible;

  - The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

    Proceed to Section A1.6.
    For Option d) proceed as in Section A1.4.

A1.6 PROCEDURE FOR LMDL DETERMINATION

- ❑ Take eight aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units.

If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. Calculate a result (x) for each sample/blank pair.

- ❑ For option c) and d), 8 replicates of a typical low level sample or spiked reagent water, calculate the standard deviation (S) of the replicate measurements as follows:

$$S = \sqrt{\left[\frac{\sum (x_i - \bar{x})^2}{(n - 1)} \right]}$$

where: $x_i =$ the analytical results in the final method reporting units for the eight replicate aliquots (i = 1 to 8)

$\bar{x} =$ the average of the eight replicate measurements

- ❑ For option a) and b), assessment of historic within run replicate analysis data, calculate the standard deviation (S) of the replicate measurements as follows:

$$S = \sqrt{\left[\frac{\sum (x_1 - x_2)_i^2}{(2 n)} \right]}$$

where:

$x_1, x_2 =$ the two replicate results for each of the n replicate pairs (minimum n = 40)

- ❑ Compute the MDL as follows:

$$MDL = t_{(n-1, \alpha = 0.01)} S$$

where:

$t_{(n-1, \alpha=0.01)}$ is the Student's value appropriate for a 99% confidence level given the degrees of freedom n-1.

S = the standard deviation as determined above.

TABLES OF STUDENT'S T VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of Replicates	Degree of Freedom (n-1)	t (n-1)
7	6	3.143
8	7	2.998
9	8	2.897
10	9	2.821
11	10	2.764
16	15	2.603
21	20	2.528
26	25	2.485
31	30	2.457
∞	∞	2.369

- ❑ Recording

  Record the calculated MDL to two significant figures (e.g. 0.032). The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount of analyte was used for this determination, also record the mean recovery.

A1.7 TREATMENT OF OUTLIERS

Single Analyte Methods:

If one of the results can be shown to be an 'Outlier' by the Dixon test (described below), AND the LMDL calculated for the remaining seven replicates (3.143 times S) is less than RMDL, this latter estimate of LMDL will be accepted.

Scans:

Certain methods permit analysis of several analytes within a single 'scan'. The MDL for each analyte in the scan must be less than the corresponding RMDL. When the LMDLs tend to bracket the RMDLs, the overall method is not sensitive enough and the LMDLs will not be considered acceptable.

However, if only a few of the LMDLs in a 'scan' exceed their respective RMDLs, there may be outliers within the set of eight replicates for these non-complying analytes. If this can be confirmed, as described above, for each of the non-complying analytes, then the LMDL based on seven replicates (3.143 times S) will be accepted for those few analytes.

To forestall the possibility that one replicate sample may be an outlier for all or most analytes in the scan, and that the calculated LMDLs therefore will be greater than RMDL for several analytes, the analyst may choose the following option:

- ❑ perform eleven replicates (rather than eight);
- ❑ for each analyte, note which replicate gives the highest and the lowest results;
- ❑ reject the sample replicate containing the greatest number of high results;
- ❑ reject the sample replicate containing the greatest number of low results;
- ❑ reject the sample with the greatest number of high and low results; and
- ❑ calculate LMDLs for each analyte using the remaining eight replicate samples.

If this procedure fails to indicate an LMDL for each analyte which is below the respective RMDL, redefine the method (for example, larger sample aliquot, different range expansion, etc.), retrain staff, and repeat the entire procedure for estimating RMDL for all analytes in the scan. Discard all previous replicate data.

Outlier procedure: Dixon's Test for sample size; n = 8 to 10.

i) sort the replicate values from lowest to highest r_1, r_2,.....$r_{(n-1)}$, r_n;

ii) determine the difference between the suspect value and its nearest neighbour $r_1 - r_2$ (or $r_n - r_{(n-1)}$);

iii) determine the difference between the suspect value and the next to last value at the opposite end of the sorted list of values $r_1 - r_{(n-1)}$, (or $r_n - r_2$);

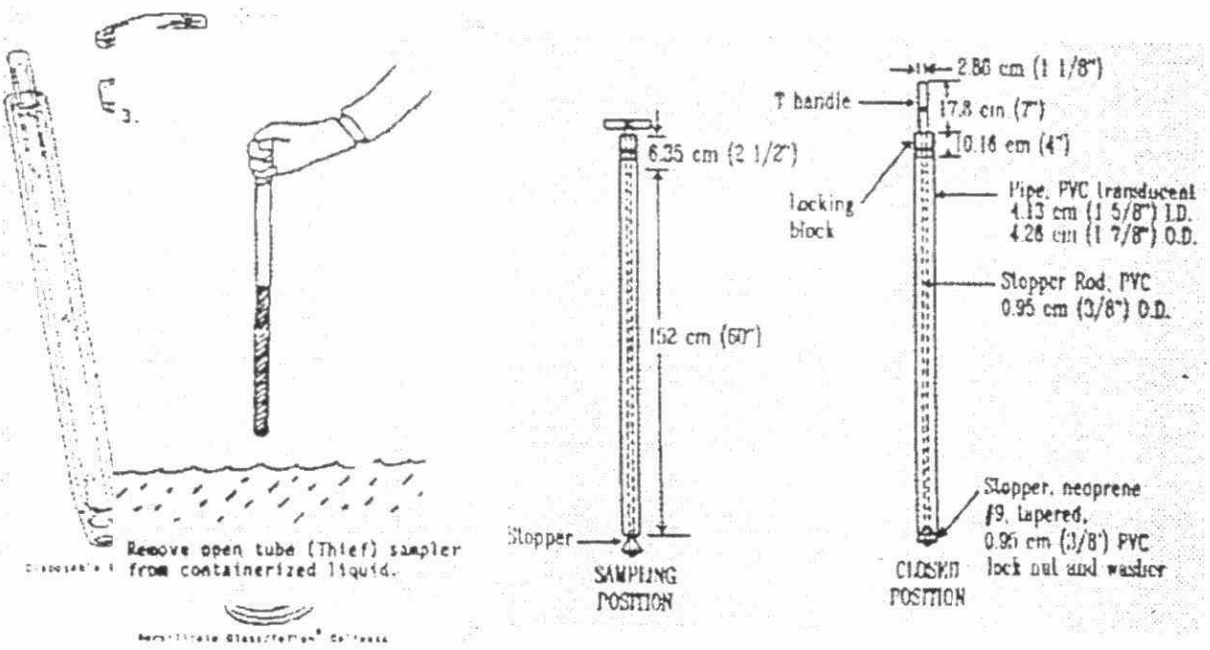
iv) calculate the ratio of ii) divided by iii);

v) if the ratio is greater than 0.55 the value r_1 (or r_n) is considered to be an outlier (<5% risk of error).

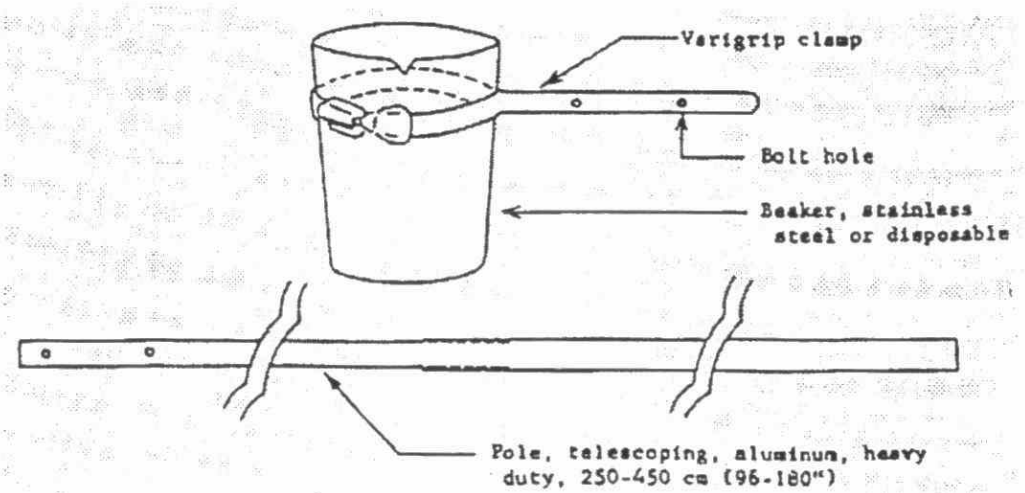
Natrella, M.G. "Experimental Statistics", NBS Handbook 91, (1966) USGPO, Washington, D.C.

APPENDIX A2: EQUIPMENT DIAGRAMS

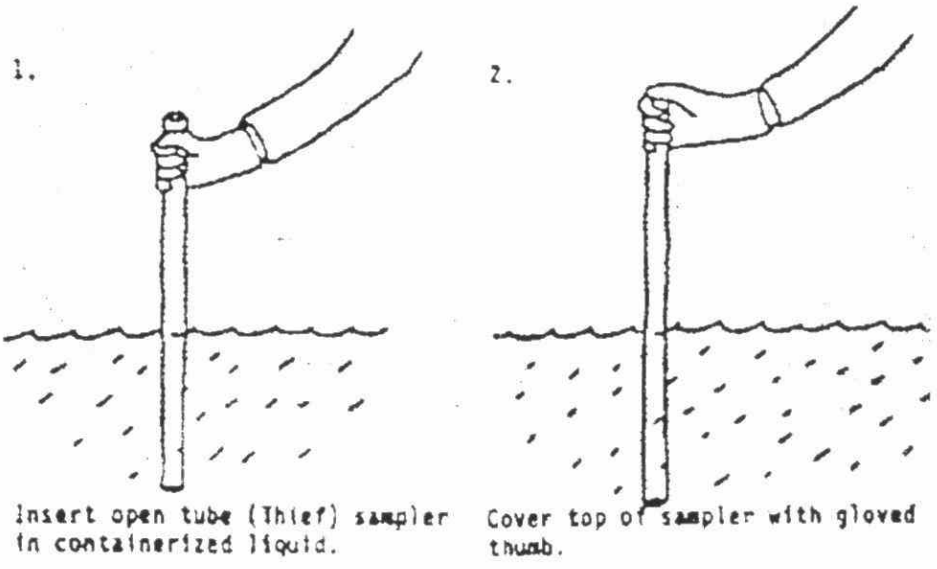
Sampling Device Name	Page
1. Coliwasa	88
2. Pond Sampler	88
3. Open Tube (Thief) Sampling	89
4. Thief	89
5. Wheaton	90
6. Bucket Auger	90
7. Scoop or Trowel	91
8. Coring Device	91
9. Silver Bullet Sampler	92
10. Veihmeyer Sampler	92
11. Ponar Dredge	93
12. PACS Sludge Getter	93
13. Hand Corer	94
14. Gravity Corer	94
15. Grain Sampler	95
16. Waste Pile Sampler	95
17. Sampling Trier	96
18. Dipper	96
19. Weighted Bottle Sampler	97
20. PACS Wide–Mouth Sampler	97
21. PACS Narrow Mouth Sampler	98
22. Stratified Sample Thief	99



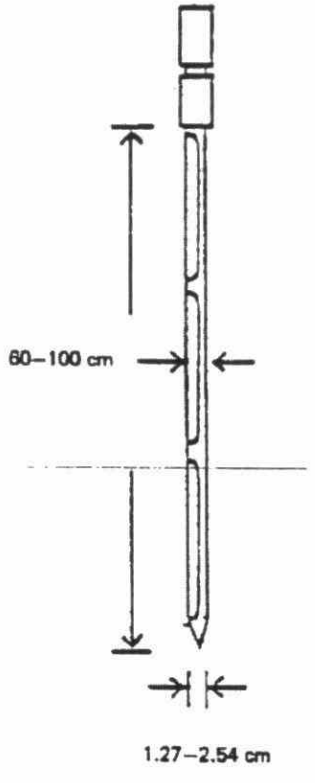
COLIWASA



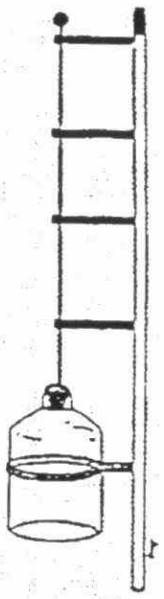
POND SAMPLER



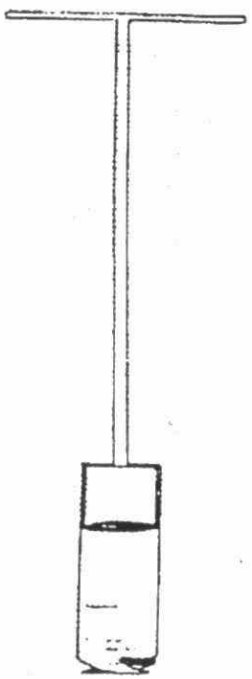
OPEN TUBE (THIEF) SAMPLING



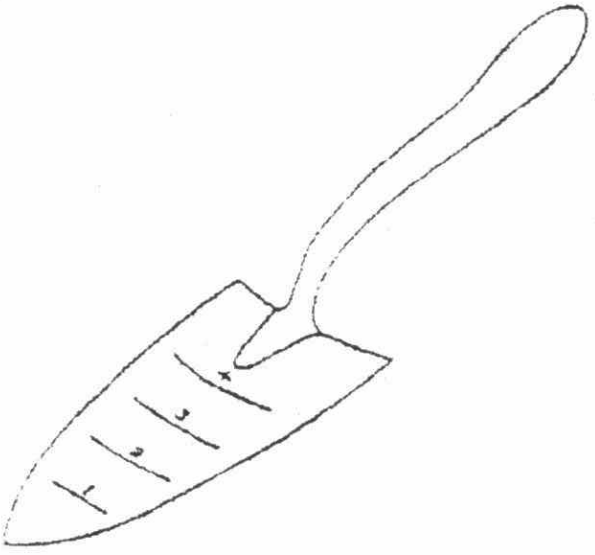
THIEF



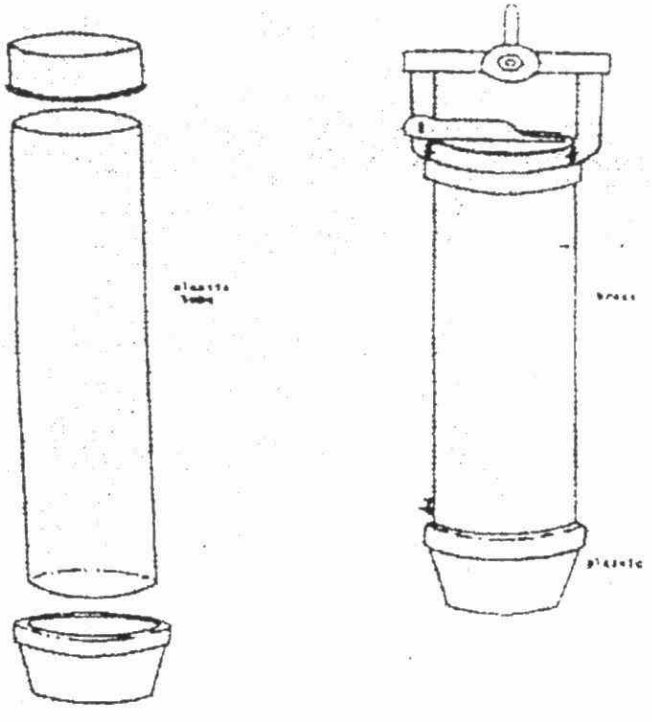
WHEATON SAMPLER



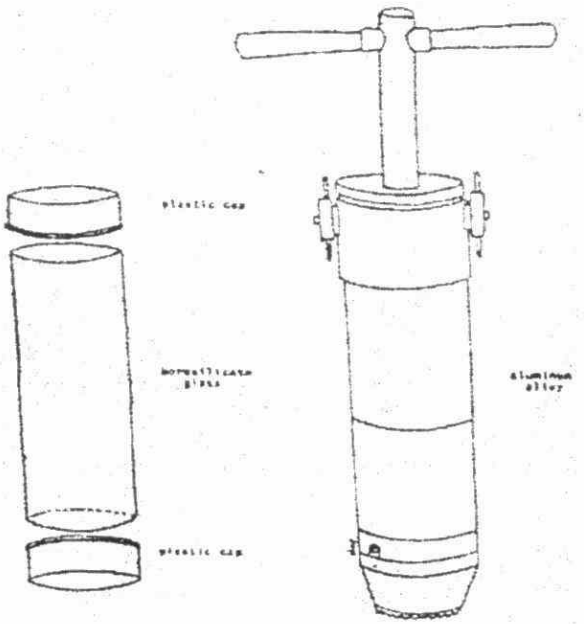
BUCKET AUGER



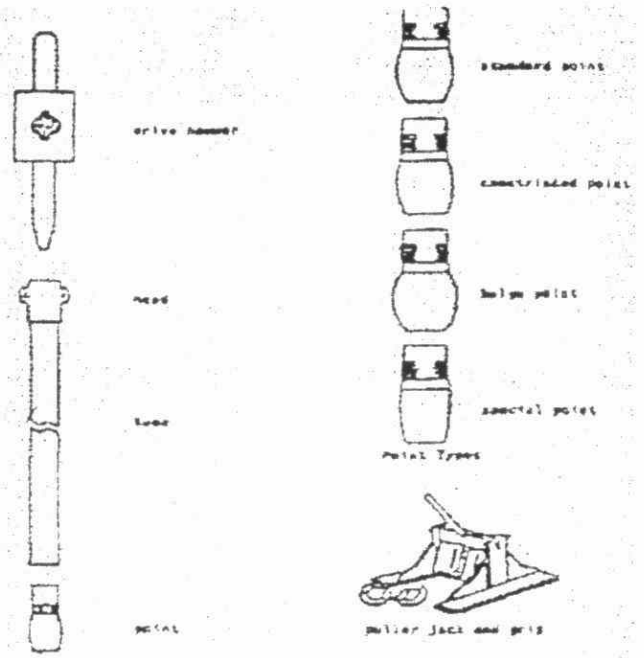
SCOOP OR TROWEL



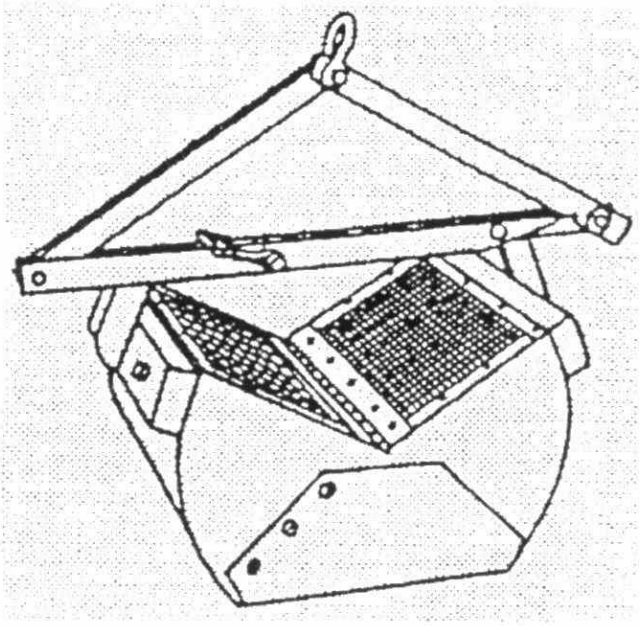
CORING DEVICE



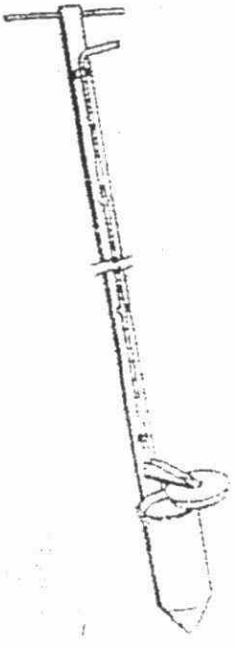
SILVER BULLET SAMPLER



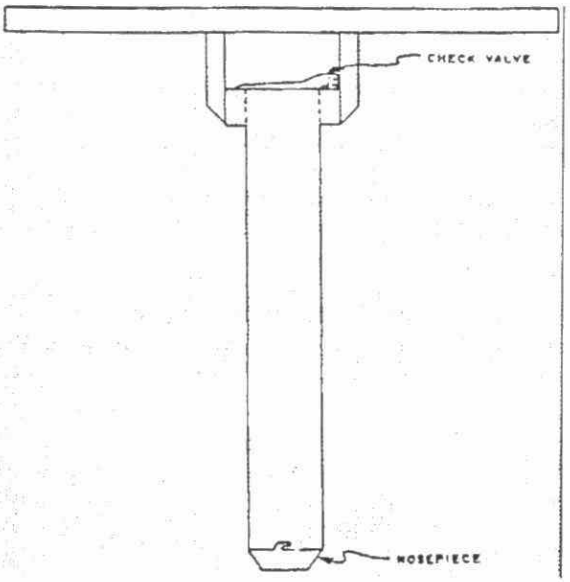
VEIHMEYER SAMPLER



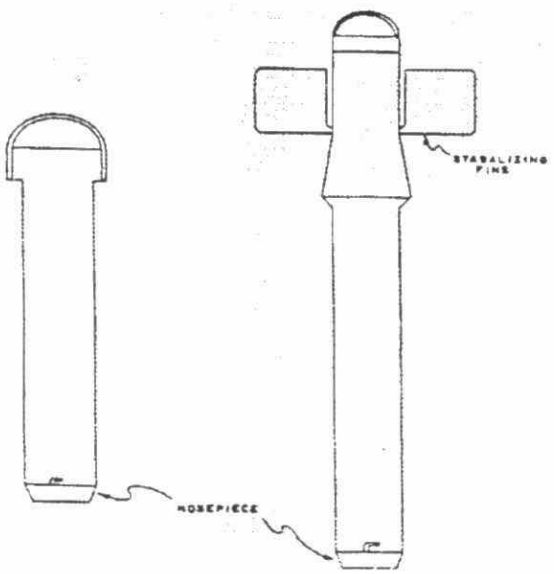
PONAR DREDGE



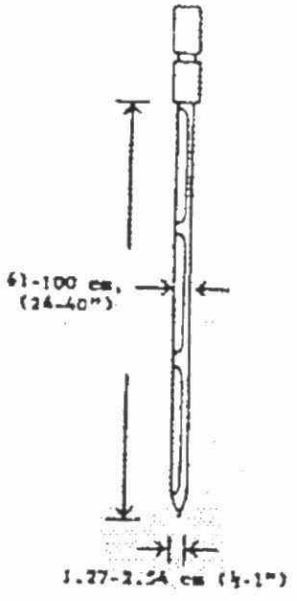
PACS SLUDGE GETTER



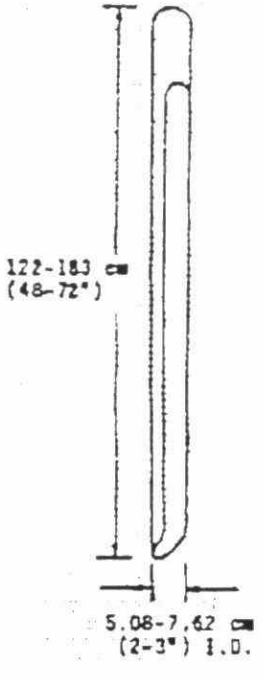
HAND CORER



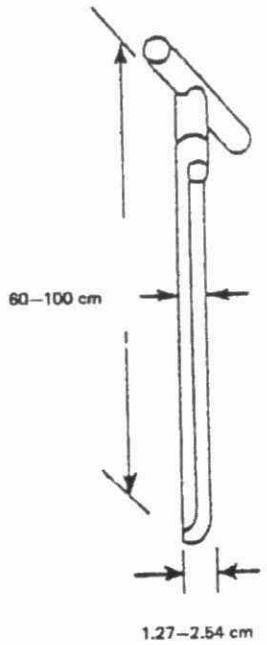
GRAVITY CORER



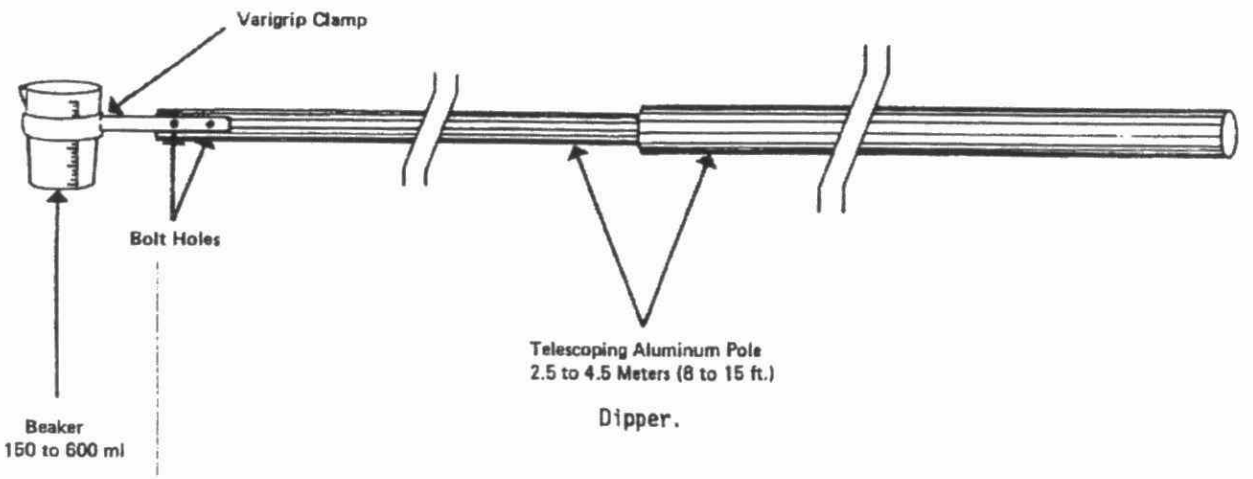
GRAIN SAMPLER



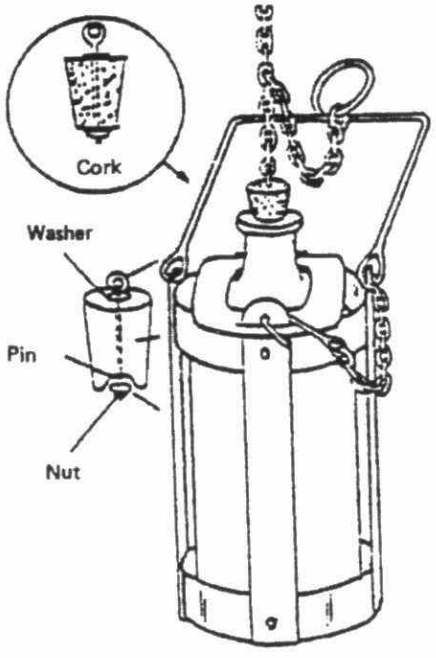
WASTE PILE SAMPLER



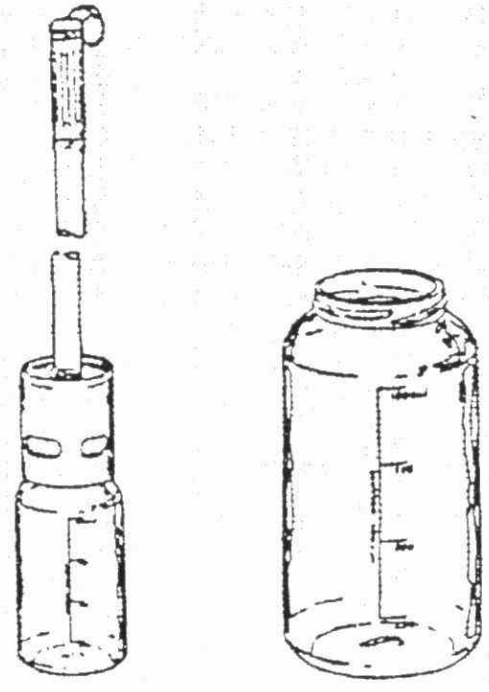
SAMPLING TRIER



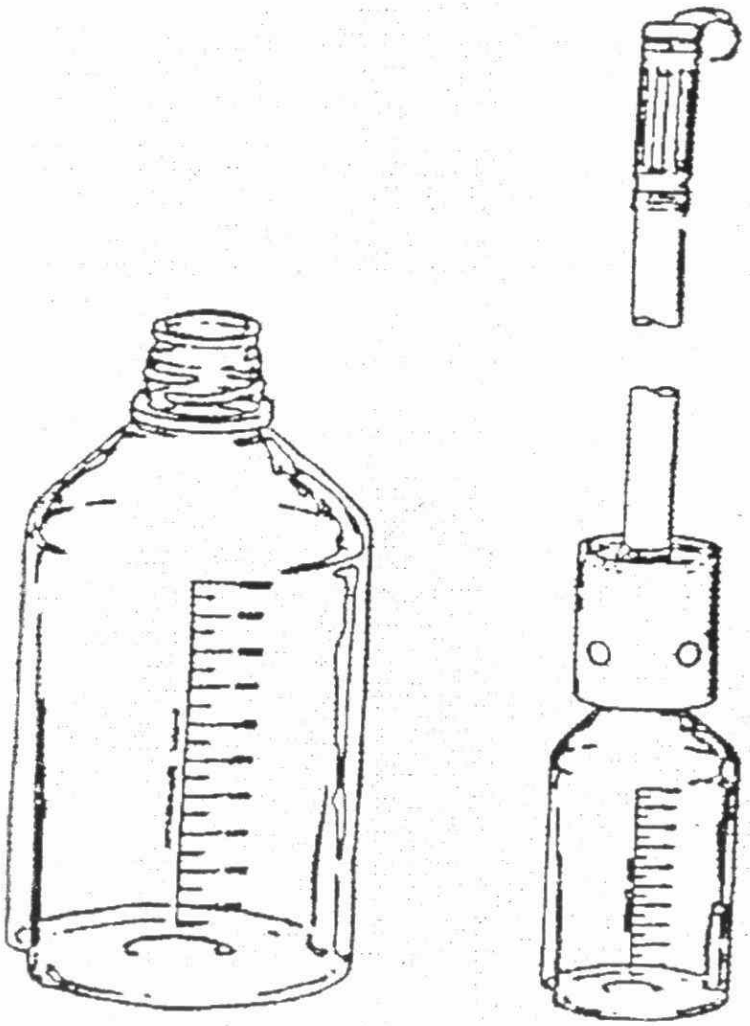
DIPPER (SEE POND)



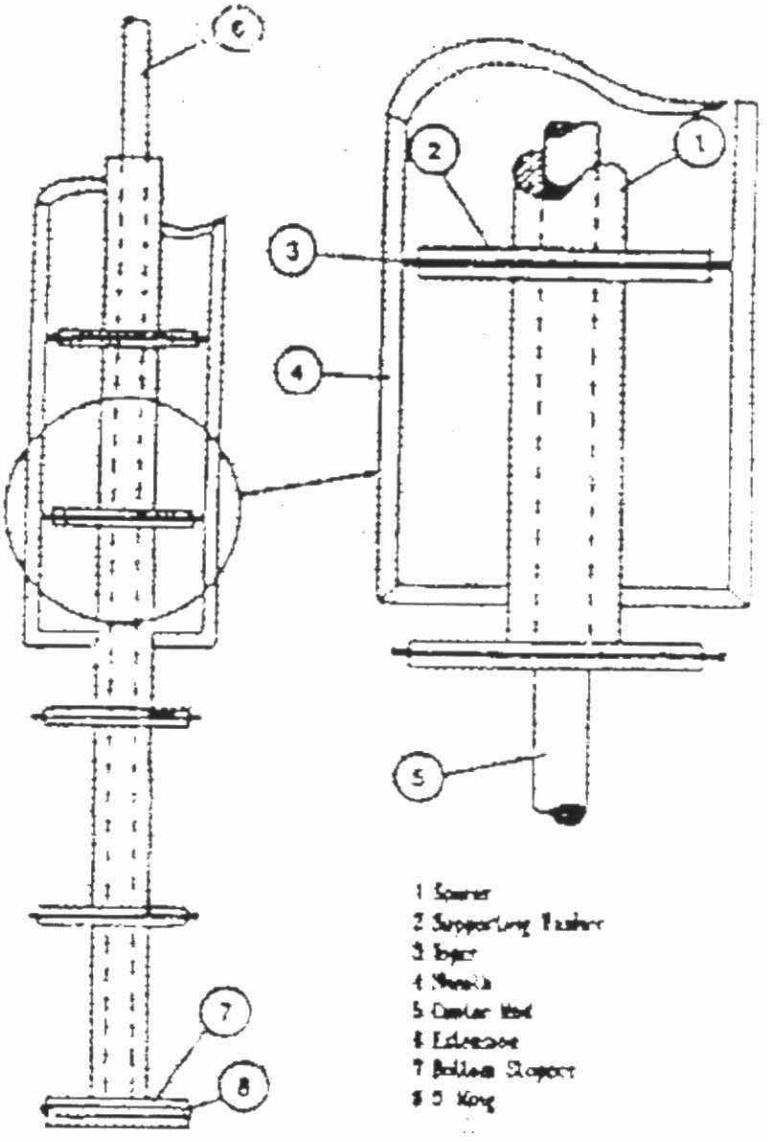
WEIGHTED BOTTLE SAMPLER



PACS WIDE–MOUTH SAMPLER



PACS NARROW–MOUTH (GRAB) SAMPLER



STRATIFIED SAMPLE THIEF

TD
193
.T69
O56
1992

Principles of sampling and
analysis of waste for TCLP :
under Ontario regulation 347 /
76905